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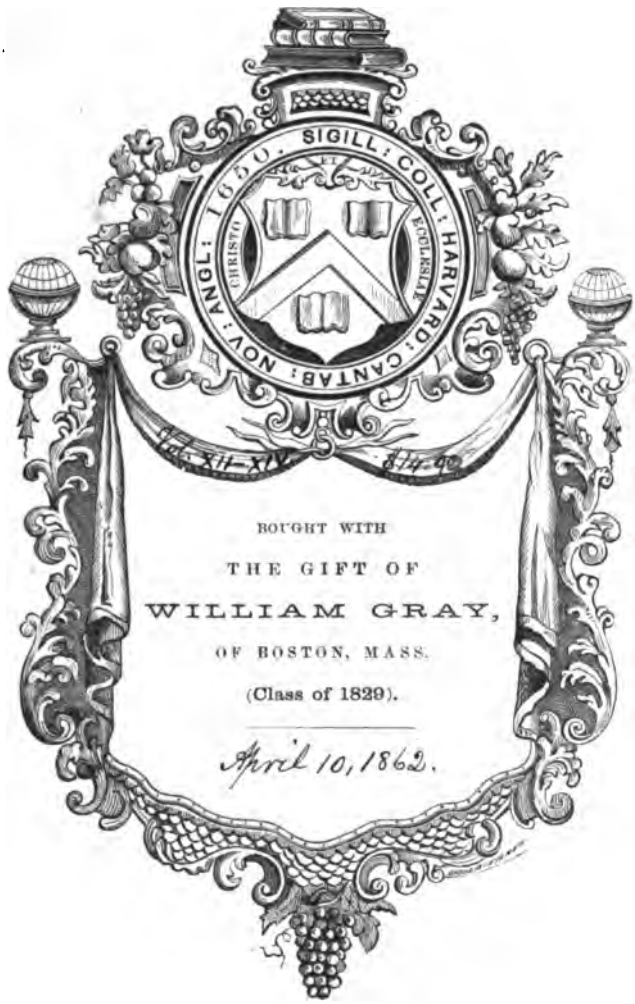


BOUGHT WITH
THE GIFT OF
WILLIAM GRAY,
OF BOSTON, MASS.
(Class of 1829).
April 10, 1862.

33·64·7

# WORKS

OF THE

# CAVENDISH SOCIETY.

FOUNDED 1846.

# HAND-BOOK

OF

# CHEMISTRY.

BY

LEOPOLD GMELIN.

VOL. XII.

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## ORGANIC CHEMISTRY,

VOL. VI.

ORGANIC COMPOUNDS CONTAINING FOURTEEN ATOMS OF CARBON.

---

TRANSLATED BY

HENRY WATTS, B.A., F.C.S.

LONDON:
PRINTED FOR THE CAVENDISH SOCIETY.

MDCCCLVIII.

~~Chem 428.48.2~~

KPE 2575

XII - XIV.
1862, Apr. 10.
314.92
Gray Fund.

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| Page. | | Line. | | | | | |
|---|---|---|---|---|---|---|---|
| 49 | .. | 27 | from top, | *for* | 85·56 | *read* | 55·86. |
| 51 | .. | 13 | from top, | ,, | 950 950 | ,, | 975 975. |

## ERRATA IN VOL. XII.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 1 | .. | 5 | from top, | *for* | $C^{14}H^{2}X^{2},O^{2}$ | *read* | $C^{14}H^{2}X^{2},O^{4}$. |
| 7 | .. | 14 | from top, | ,, | $H^{14}$ | ,, | $H^{4}$. |
| 44 | .. | 18 | from bottom, | ,, | Hg | ,, | Ag. |
| 47 | .. | 15 | from top, | ,, | $H^{8}$ | ,, | $H^{6}$. |
| 76 | .. | 11 | from bottom, | ,, | $O^{8}$ | ,, | $O^{6}$. |
| 96 | .. | 18 | from top, | ,, | $C^{28}$ | ,, | $C^{24}$. |
| 114 | .. | 15 | from bottom, | ,, | lead | ,, | lime. |
| 132 | .. | 22 | from bottom, | ,, | $C^{14}XH^{4}O$ | ,, | $C^{14}XH^{4}O^{3}$. |
| 189 | .. | 6 | from bottom, | ,, | $C^{16}$ | ,, | $C^{26}$. |
| 246 | .. | 16 | from top, | ,, | $H^{4}$ | ,, | $H^{6}$. |
| 262 | .. | 9 | from bottom, | ,, | $C^{14}BrH^{7}O^{3}$ | ,, | $C^{14}BrH^{7}O^{2}$. |
| 272 | .. | 2 | from top, | ,, | $H^{18}$ | ,, | $H^{10}$ |
| 291 | .. | 1 | from top, | ,, | Br | ,, | $Br^{3}$. |
| 291 | .. | 10 | from bottom, | ,, | $O^{7}$ | ,, | $H^{7}$ |
| 297 | .. | 20 | from bottom, | ,, | $ClH^{5}$ | ,, | $Cl^{2}H^{4}$. |
| 298 | .. | 2 | from top, | ,, | $C^{14}Cl^{2}H^{4}O^{2},O^{2}$ | ,, | $C^{14}Cl^{2}H^{4}O^{2},O^{4}$. |
| 313 | .. | 11 | from top, | ,, | $O^{6}$ | ,, | $O^{10}$. |
| 313 | .. | 12 | from top, | ,, | $O^{5}$ | ,, | $O^{9}$. |
| 400 | .. | 13 | from top, | ,, | $H^{8}$ | ,, | $H^{6}$. |
| 406 | .. | 6 | from top, | ,, | $O^{18}$ | ,, | $O^{10}$. |
| 465 | .. | 4 | from top, | ,, | $C^{10}$ | ,, | $C^{14}$. |

# COMPOUNDS CONTAINING 14 AT. CARBON.

*Primary Nucleus* $C^{14}H^{4}$.

*Nitro-nucleus* $C^{14}X^{2}H^{2}$.

## Chrysammic Acid.

$C^{14}H^{2}N^{2}O^{12} = C^{14}X^{2}H^{2},O^{2}$.

BRACONNOT. *Ann. Chim.* 68, 28.
CHEVREUL. *Ann. Chim.* 73, 46; also *Gilb.* 44, 159.
LIEBIG. *Schw.* 49, 387; *Pogg.* 13, 205.
BOUTIN. *J. Pharm.* 26, 184; also *N. Br.* 23, 294.
SCHUNCK. *Ann. Pharm.* 39, 1; 65, 234.
ROBIQUET. *N. J. Pharm.* 10, 178.
MULDER. *Scheik. Onderz.* 4, 516; 5, 173; abstr. *J. pr. Chem.* 42, 250; 48, 1.

From χρυσὸς and ἄμμος (sand).
*Aloetic acid, Polychromatic acid, Artificial Bitter of Aloes, Aloesäure, Aloetinsäure.*

*Formation.* By the action of hot nitric acid upon alöin. (Stenhouse, *Ann. Pharm.* 77, 208.) Apparently also by the action of nitric acid upon aporetin, one of the constituents of rhubarb. (De la Rue & Müller, *Chem. Soc. Qu. J.* 10, 306.)

*Preparation.* 1 pt. of aloes is gently heated in a capacious flask with 8 pts. of strong nitric acid, till gas begins to escape. In this action, according to Boutin, a peculiar substance is given off, which he calls *cyanyl*, which, however, according to Robiquet, is a mixture of hydrocyanic and formic acids in varying proportions. The liquid begins to boil violently after being removed from the fire. As soon as the evolution of gas has ceased, the mixture is introduced into a retort and the nitric acid distilled off, 3 or 4 pts. more of strong nitric acid then added, and the distillation repeated; the residual liquid mixed with water till no further precipitate is thereby produced; and the precipitate, consisting of small shining scales, is washed with cold water till the water acquires from it no longer a yellow

but a faint purple-red colour. The resulting chrysammic acid, still containing aloetic acid, is triturated with aqueous carbonate of potash; and the gelatinous mass, which is thereby formed, with evolution of carbonic acid, is washed with cold water till the whole of the carbonate of potash is removed, then dissolved in boiling water, and the solution filtered; as the liquid cools, the pure potash-salt separates in golden yellow laminæ. These crystals are dissolved in boiling water, and decomposed by nitric acid; and the chrysammic acid, which separates in the form of a yellow powder, is washed with cold water, till the nitric acid is completely removed, and the water is coloured no longer yellow, but light purple-red. In treating the chrysammic acid with carbonate of potash, an excess of the latter must be avoided as far as possible, because it produces a decomposition and reddening of the salt (from admixture of aloetic acid?). The same decomposition occurs when the acid, as Schunck recommends, is boiled with carbonate of potash.

*Properties.* Yellow powder, often light yellow or greenish yellow, consisting of small shining scales. (Schunck.) Boutin's polychromatic acid was dark red brown. A mixture of aloetic or aloeretic acid gives to chrysammic acid an orange tinge. By boiling with sulphuric acid, it is converted into a green modification. (Mulder.) The acid when slowly heated in contact with the air, melts to a brown liquid, giving off a large quantity of gas, and diffusing a small quantity of greenish vapour. (Schunck.) It melts when heated and gives off red vapours. (Mulder.) Tastes very bitter and astringent; reddens litmus. (Braconnot, Boutin, Schunck.)

| | *Calculation.* | | Boutin. | Schunck. | Mulder. *a.* | Mulder. *b.* |
|---|---|---|---|---|---|---|
| 14 C | 84 | 40·00 | 39·4 | 39·77 | 39·80 | 40·09 |
| 2 N | 28 | 13·33 | 12·2 | 12·44 | 13·00 | 13·59 |
| 2 H | 2 | 0·95 | 1·1 | 1·20 | 1·05 | 1·06 |
| 12 O | 96 | 45·72 | 47·3 | 46·59 | 46·15 | 45·26 |
| $C^{14}N^2H^2O^{12}$ | 210 | 100·00 | 100·0 | 100·00 | 100·00 | 100·00 |

*Decompositions.* 1. The acid, heated in a glass tube sealed at the bottom, melts with copious evolution of gas, but detonates immediately afterwards with a bright flash, filling the tube completely with soot and emitting a strong odour of hydrocyanic and nitrous acids. (Schunck.) It detonates when suddenly heated (Braconnot, Chevreul), between 300° and 400°, according to Boutin, giving off carbonic oxide, carbonic acid, nitrogen, olefiant gas, hydrocyanic acid, and charcoal (Chevreul, Boutin), emitting the odour of formic, hydrocyanic and nitrous acids, and yielding a large quantity of charcoal. (Mulder.) — 2. When quickly heated in contact with the air, it detonates violently, and burns with a bright, very sooty flame, leaving a very difficultly combustible charcoal. (Schunck.)

3. Dry *chlorine* gas does not act upon the acid at ordinary temperatures, but eliminates hydrochloric acid on the application of heat. (Schunck.) — 4. It is dissolved by strong *nitric acid*, especially by the fuming acid, and on boiling, is slowly converted into picric acid. — 5. By distillation with *chloride of lime* and water, it yields chloropicrin. (Stenhouse.) — 6. Oil of vitriol does not act upon the acid at ordinary temperatures; but at a boiling heat it eliminates hyponitric acid, sulphurous acid, carbonic oxide, and carbonic acid, and separates violet chry-

iodin. — 7. Chrysammic acid dissolves in 3 or 4 pts. of dilute sulphuric acid; water added to the brown solution throws down a green powder (Robiquet's *chrysammelide*) consisting of pure chrysammic acid, which has merely assumed a different state of aggregation, as shown by Mulder's analysis *b*. Chrysammic acid is not altered by boiling with very dilute hydrochloric or sulphuric acid.

8. When chrysammic acid is boiled with *potash*-ley, carbonate of potash, baryta-water, or lime-water, a black-brown liquid is produced containing chrysatric acid. — 9. *Hydrosulphate of ammonia* imparts to it a beautiful violet colour, which changes to indigo-blue when heated, from formation of chrysindamide and a compound of chrysindin with oxide of ammonium. — 10. When *sulphurous acid* in excess is passed into a solution of chrysammic acid in ammonia, the liquid turns brown, and does not yield any precipitate when treated with hydrochloric acid; if an excess of sulphurous acid be avoided, the liquid acquires a fine violet colour, and hydrochloric acid throws down from it a brown jelly. (Mulder.) — 11. *Protochloride of tin* colours the aqueous acid violet after a while, the colour changing to indigo-blue when the liquid is heated.

*Combinations.* Chrysammic acid dissolves sparingly in cold water (in 125 pts. according to Braconnot, in more than 800 pts. according to Liebig), forming a light red solution; more abundantly in hot water (in 850 pts. of water at 100°, according to Boutin), forming a purple-red solution; the solution is coloured yellow by nitric or hydrochloric acid. In nitric acid and other mineral acids it is somewhat more soluble than in water. In saline solutions, also, it dissolves more abundantly than in cold water. (Mulder.)

Chrysammic acid has for salifiable bases, as strong an affinity as oxalic acid. The *chrysammates* are all yellow, mostly crystallise in small needles or scales, and exhibit on the crystalline faces a gold-green metallic lustre; the amorphous chrysammates exhibit the same lustre when rubbed with a hard body. They detonate violently when heated, but less so than the picrates. They are all, even those of the alkalies, but very sparingly soluble. In acetates they dissolve more readily than in pure water, but less when heated than in the cold.

*Chrysammate of ammonia* does not appear to exist, inasmuch as chrysammic acid and ammonia immediately form chrysammide.

*Chrysammate of Potash.* — *Preparation,* p. 1. — Crystallises on cooling from a hot solution, in gold-green laminæ exhibiting the most splendid iridescence; when quickly cooled, it separates as an amorphous red powder. The powder is easily burnished upon glass, and then exhibits a remarkable dichroïsm, both by transmitted and by reflected light. By transmitted light polarised in the direction of the streak, its colour varies from flesh-red to blood-red; at right angles to the streak, from carmine to crimson; by reflected light polarised in the direction of the streak: steel-grey, passing into violet, or at greater angles of incidence, violet to deep indigo; at right angles to the streak, brass-yellow, or at greater angles of incidence, metallic green to dark steel-blue. (Brewster, Haidinger, *Wien. Akad. Ber.* 8, 97.) — Heated to 120° in a current of dry air, the salt gives off 9·5 per cent. of water (3 At. calculated quantity 9·8). Mulder.

| | | | Schunck. | Mulder. |
|---|---|---|---|---|
| KO | 47·2 | 19·02 | 17·88 | 18·9 |
| 14 C | 84·0 | 33·84 | 34·55 | 34·1 |
| H | 1·0 | 0·40 | 0·95 | 0·8 |
| 2 N | 28·0 | 11·28 | 10·69 | 11·2 |
| 11 O | 88·0 | 35·46 | 35·93 | 35·0 |
| $C^{14}N^2HKO^{12}$ | 248·2 | 100·00 | 100·00 | 100·0 |

Schunck deduced from his own analysis, the formula $KO,C^{15}N^2H^2O^{12}$, but overlooked the water.

The salt detonates when heated, emitting the same odour as the acid — It dissolves sparingly in cold water (in 1250 pts. according to Schunck); in boiling water it dissolves pretty easily, forming a fine red solution.

*Chrysammate of Soda.* — The aqueous acid immediately forms with acetate of soda, a red jelly, which, after washing with cold water, dissolves in boiling water, and the solution, if quickly cooled, deposits the soda-salt, in the form of a red, or sometimes a greenish yellow powder; by slow cooling it is obtained in crystals. — Gives off 11·6 p. c. (3 At.) water at 155°. (Mulder.) It is as sparingly soluble in water as the potash-salt.

| | | Mulder. |
|---|---|---|
| $C^{14}N^2HO^{11}$ | 76·2 | 76·11 |
| NaO | 12·2 | 11·97 |
| 3 HO | 11·6 | 11·92 |
| $C^{14}N^2HNaO^{12}$ + 3Aq | 100·0 | 100·00 |

*Chrysammate of Baryta.* — Formed by mixing a solution of chloride of barium, drop by drop, with a boiling solution of chrysammate of potash. Heavy precipitate of a fine vermillion colour. When rubbed with a hard substance, it acquires a yellow golden lustre. Insoluble in water. Detonates when heated. (Schunck, Mulder.) Contains 13·9 p. c. (5 At.) water, of which only 3 At. are given off at 110°; to render it anhydrous, it must be heated for a long time to 154°. (Mulder.)

| | | Schunck. | Mulder *at* 110°. |
|---|---|---|---|
| BaO | 25·9 | 25·55 | 25·91 |
| 14 C | 28·5 | 30·38 | 28·80 |
| 2 N | 9·5 | 9·51 | |
| 3 H | 1·0 | 1·24 | 1·41 |
| 13 O | 35·1 | 33·32 | |
| $C^{14}N^2HBaO^{12}$ + 2Aq | 100·0 | 100·00 | |

*Chrysammate of Strontia.* — A solution of a nitrate of strontia is added by drops to a warm aqueous solution of chrysammic acid or chrysammate of potash. Light purple salt more soluble than the baryta-salt. (Mulder.)

*Chrysammate of Lime.* — Obtained by decomposing a warm solution of chrysammate of potash with chloride of calcium, or by heating acetate

of potash with chrysammic acid. Dark red, somewhat crystalline powder. (Schunck, Mulder.) — After drying in the air, it gives off 20 p. c. (6 At. water) at 145°. (Mulder.)

| | | | Mulder. |
|---|---|---|---|
| $C^{14}N^2HO^{11}$ | 71·1 | | 70·4 |
| CaO | 9·9 | | 9·4 |
| 6 HO | 19·0 | | 20·2 |
| $C^{14}N^2HCaO^{12}$ + 6Aq | 100·0 | | 100·0 |

*Chrysammate of Magnesia.* — Prepared like the baryta-salt. Light red powder, soluble with tolerable facility in hot water. After drying in the air, it contains 19·6 per cent. of water, the whole of which is given off at 154°. (Mulder.)

*Chromic Chrysammate* is of a dirty brown colour, and sparingly soluble.

*Chrysammate of Manganese.* — Obtained by decomposing acetate of manganese with chrysammic acid. Has a fine red colour; dissolves in water with tolerable facility. After drying in the air, it contains 16 per cent. (5 At.) of water, which goes off at 145°. (Mulder.)

| | | | | Mulder. |
|---|---|---|---|---|
| $C^{14}N^2HO^{11}$ | 201·0 | 71·3 | | 71·16 |
| MnO | 35·6 | 12·7 | | 12·29 |
| 5 HO | 45·0 | 16·0 | | 16·65 |
| $C^{14}N^2HMnO^{12}$ + 5Aq | 281·6 | 100·0 | | 100·00 |

*Chrysammate of Zinc.* — Chrysammate of potash forms with sulphate of zinc a very sparingly soluble precipitate of a fine purple-red colour. (Mulder.) Small dark-red needles having a golden lustre. (Schunck.)

*Chrysammate of Cadmium.* — Aqueous chrysammic acid is not precipitated by nitrate of cadmium. Chrysammate of potash forms with nitrate of cadmium a dark purple precipitate soluble in water. (Mulder.)

*Chrysammate of Lead.* — *a. Monobasic.* — Obtained by double decomposition of chrysammate of potash with a soluble lead-salt, or by treating neutral acetate of lead with a warm solution of chrysammic acid. (Mulder.) — Brick-red powder. (Schunck.) Insoluble in water. Gives off 12·6 p.c. (5 At.) water at 155°. (Mulder.)

| | | | | Schunck. | Mulder *at* 155°. |
|---|---|---|---|---|---|
| PbO | 111·8 | 35·74 | | 34·19 | 35·6 |
| 14 C | 84·0 | 26·85 | | 26·82 | |
| 2 N | 28·0 | 8·95 | | 8·40 | |
| H | 1·0 | 0·32 | | 0·78 | |
| 11 O | 88·0 | 28·14 | | 29·81 | |
| $C^{14}N^2HPbO^{12}$ | 312·8 | 100·00 | | 100·00 | |

*b. Bibasic.* — Obtained by dropping a hot solution of chrysammate of potash into an aqueous solution of neutral acetate of lead. Dark

red precipitate, which becomes lighter in colour and granular when heated. (Mulder.)

| | | | Mulder at 120°. |
|---|---|---|---|
| 2 PbO | 233·6 | 51·57 | 51·61 |
| 14 C | 84·0 | 19·37 | 20·28 |
| 2 N | 28·0 | 6·45 | 6·20 |
| 2 H | 2·0 | 0·46 | 0·61 |
| 12 O | 96·0 | 22·15 | 21·30 |
| $C^{14}N^2HPbO^{12}$ + PbO,HO.. | 443·6 | 100·00 | 100·00 |

*Ferrous* and *Ferric Chrysammates.*—Obtained by double decomposition. Deep violet-coloured, dissolving with tolerable facility in water. (Mulder.)

Chrysammate of potash forms with *Cobalt-salts* a brownish yellow, sparingly soluble precipitate; in nickel-salts, a sparingly soluble precipitate of a fine purple colour.

*Chrysammate of Copper.*—By dropping a warm solution of chrysammate of potash into a solution of sulphate of copper, a dark red powder is precipitated. (Schunck, Mulder.) It dissolves in hot more readily than in cold water, and crystallises from the boiling solution on cooling, in dark purple-red needles having a yellow golden lustre. (Schunck.) If the potash salt was not free from aloetic or aloeretic acid, the wash-water acquires a violet colour. (Mulder.)

| | | | Mulder at 120°. |
|---|---|---|---|
| $C^{14}N^2HO^{11}$ | 201·0 | 83·56 | |
| CuO | 39·8 | 16·44 | 16·45 |
| $C^{14}N^2HCuO^{12}$ | 240·8 | 100·00 | |

*Tetrahydrated Chrysammate of Copper.*—Pure chrysammic acid is triturated with acetate of copper, and the mixture digested for some time at 80°. At 150°, or when dried for a considerable time at 100°, the salt gives off 13·4 per cent. of water. (Mulder.)

| | | | Mulder. |
|---|---|---|---|
| $C^{14}N^2HCuO^{12}$ | 240·8 | 86·6 | |
| 4 HO | 36·0 | 13·4 | 13·7 |
| $C^{14}N^2HCuO^{12}$ + 4Aq | 276·8 | 100·0 | |

*Mercurous Chrysammate.*—Purple-red, sparingly soluble in water.

A solution of chrysammate of potash is not precipitated by solution of corrosive sublimate.

*Chrysammate of Silver.*—Dark brown, somewhat crystalline. Streak golden yellow. (Schunck.) Dark violet crystalline needles, sparingly soluble in cold water, readily in hot. (Boutin.) Dark violet, nearly insoluble in water. (Mulder.)

*Chrysammate of Gold.* — Precipitated from gold solutions by chrysammate of potash; yellowish brown. Dissolves in hot water without change of colour, but is nearly insoluble in cold water. (Mulder.)

*Chrysammate of Platinum.* — Yellow. — Obtained by dropping a platinum solution into a warm solution of chrysammic acid, or by double decomposition of chrysammate of soda with chloride of platinum. (Mulder.)

In *alcohol* and in *ether*, chrysammic acid dissolves more readily than in water. (Schunck.) It dissolves in 70 to 80 pts. of cold alcohol of 36°. (Boutin.)

It imparts to silk and wool a very fine and permanent crimson, violet, or blue colour, according to the mordant used. (Boutin.)

## Chrysammide.

$$C^{14}N^3H^{14}O^{11} = C^{14}HAdX^2O^2,HO.$$

SCHUNCK. *Ann. Pharm.* 39, 22; 65, 236.
ROBIQUET. *N. J. Pharm.* 10, 177.
MULDER. *Scheik.* 4, 486; 5, 184; abstr. *J. pr. Chem.* 48, 5.

*Chrysammamsäure, Chrysamminamide.*

*Preparation.* 1. Dry ammoniacal gas is passed over dry chrysammic acid at 100°, the acid then giving off water and assuming a deep violet colour. (Mulder.) — 2. Chrysammic acid is dissolved in boiling ammonia, and the dark purple solution left to cool, whereupon the chrysammide crystallises out. (Schunck.) — Chrysammic acid is treated with excess of ammonia, and the resulting violet-red jelly washed with water and dried at 100°. (Mulder.) The chrysammide obtained by boiling chrysammic acid with ammonia, is contaminated with chrysatric acid. (Mulder.)

*Properties.* Green needles having a metallic lustre, reddish brown by transmitted light. (Schunck.) Dark violet amorphous powder; crystallises from solution in hot water in violet-gold-green laminæ. (Mulder.)

| | | | Schunck. | Mulder. |
|---|---|---|---|---|
| 14 C | 84 | 38·53 | 37·21 | 37·81 |
| 3 N | 42 | 19·27 | 19·81 | 19·15 |
| 4 H | 4 | 1·83 | 2·28 | 2·07 |
| 11 O | 88 | 40·37 | 40·70 | 40·97 |
| $C^{14}N^3H^4O^{11}$ | 218 | 100·00 | 100·00 | 100·00 |

According to this, the formation of chrysammide would be attended, contrary to the general rule, with the separation of only 1 At. water:

$$C^{14}N^2H^2O^{12} + NH^3 = C^{14}N^3H^4O^{11} + HO.$$

Mulder found, that, in the preparation of chrysammide by the first process, the chrysammic acid lost 4·4 per cent. of water, the quantity required by calculation being 4·3. — Schunck leaves it undecided whether his chrysammide should have the formula $C^{28}N^7H^{10}O^{21}$ or $C^{30}N^7H^{10}O^{22}$. As chrysammide combines with bases, Mulder is of opinion that Schunck's preparation contained ammonia.

*Decompositions.* 1. Strong *hydrochloric acid* does not act on chrysammide at ordinary temperatures, but when heated with it, produces sal-ammoniac and chrysammic acid. — 2. By continued action of strong *nitric acid,* in the cold, or by boiling the aqueous solution with nitric acid, chrysammide is reconverted into chrysammic acid. (Schunck, Mulder.) — 3. Cold *oil of vitriol* dissolves chrysammide, forming a yellow solution; and if this solution be immediately mixed with a large quantity of water, the liquid assumes a beautiful violet colour, and deposits the greater part of the chrysammide in the unaltered state. If the yellow solution in oil of vitriol be mixed with a small quantity of water and heated, it loses its colour and deposits chrysammic acid in the form of a greenish yellow powder. When oil of vitriol has acted upon chrysammic acid for a long time, the violet colour is not reproduced by water; and on heating the liquid, chrysammic acid separates out. (Mulder.)

According to Schunck (*Ann. Pharm.* 66, 237) when hydrochloric or sulphuric acid is added to a hot aqueous solution of chrysammide, the liquid on cooling, yields dark olive-green needles of *amido-chrysammic acid,* whose composition is either $C^{14}N^3H^4O^{11}$ (the same as that of chrysammide) or $C^{15}N^3H^4O^{12}$.

| *Calculation I.* | | | *Calculation II.* | | | Schunck. |
|---|---|---|---|---|---|---|
| 14 C | 84 | 38·53 | 15 C | 90 | 38·74 | 38·72 |
| 4 H | 4 | 1·83 | 4 H | 4 | 1·72 | 1·88 |
| 3 N | 42 | 19·27 | 3 N | 42 | 18·27 | 18·26 |
| 11 O | 88 | 40·37 | 12 O | 96 | 41·27 | 41·14 |
| $C^{14}N^3H^4O^{11}$ | 218 | 100·00 | $C^{15}N^3H^4O^{12}$ | 232 | 100·00 | 100·00 |

(According to Mulder, these crystals are a mixture of chrysammide with a small quantity of chrysammic acid.) — The substance dissolves in water, forming a dark purple solution, and is not reprecipitated by strong acids. It unites with salifiable bases, forming salts, which very much resemble the chrysammates, but may be distinguished from the latter by their property of giving off ammonia when treated with caustic potash. — *Amidochrysammate of potash,* prepared by treating the acid with a cold solution of carbonate of potash, separates when recrystallised from boiling water, after the excess of carbonate of potash has been removed by washing, in small needles, possessing the metallic green lustre of chrysammate of potash. — *Amidochrysammate of Baryta* separates as a dark red crystalline powder, when a solution of chrysammide is boiled for some time with chloride of barium, and is immediately precipitated on mixing the solution of chrysammide and chloride of barium with ammonia.

| | | | Schunck. |
|---|---|---|---|
| 14 C | 84·0 | 28·53 | 29·93 |
| 4 H | 4·0 | 1·36 | 1·77 |
| 3 N | 42·0 | 14·29 | |
| 11 O | 88·0 | 30·05 | |
| BaO | 76·6 | 25·77 | 25·11 |
| $C^{14}N^3H^4O^{11}$,BaO | 294·6 | 100·00 | |

According to Mulder, the precipitate formed by boiling chrysammide with chloride of barium, consists of chrysammate of baryta, the liquid, as Schunck also found, containing sal-ammoniac; when ammonia is added to a solution of chrysammide and chloride of barium, a compound of chrysammide and baryta is deposited.

4. Strong *potash-ley* decomposes chrysammide at ordinary temperatures, with evolution of ammonia. (Mulder.) When the aqueous solution of chrysammide is boiled with potash, baryta, or lime, ammonia escapes and the liquid turns brown, yielding the decomposition-products of chrysammic acid. (Schunck, Mulder.)

*Combinations.* Chrysammide dissolves readily in water, forming a violet solution. It combines with salifiable bases. Its compounds with soda, baryta, lime, manganous oxide, zinc-oxide, cupric oxide, and silver-oxide, are soluble in water.

The compound of chrysammide with lead-oxide is produced on mixing neutral acetate of lead with a warm aqueous solution of chrysammide, which has been freed from ammonia by continued boiling: it is nearly insoluble in water. (Mulder.)

| | | | | Mulder, *at* 100°. |
|---|---|---|---|---|
| 14 C | 84·0 | .... | 17·9 | ..... 18·25 |
| 3 N | 42·0 | .... | 8·9 | |
| 7 H | 7·0 | .... | 1·4 | ..... 1·56 |
| 14 O | 112·0 | .... | 24·1 | |
| 2 PbO | 223·6 | .... | 47·7 | ..... 46·42 |
| $C^{14}N^3H^3O^{10},2PbO + 4HO$ | 468·6 | .... | 100·0 | |

When heated above 100°, it gives off ammonia, and leaves a mixture of chrysammic acid and oxide of lead. (Mulder.)

Chrysammide dissolves in *alcohol* and *ether* more readily than in water.

*Appendix to Chrysammic Acid.*

## Aloeretic Acid. $C^{14}NH^3O^{12}$.

E. Schunck. *Ann. Pharm.* 39, 24.
G. J. Mulder. *Scheik.* 5, 188; *J. pr. Chem.* 48, 14.

*Formation.* By treating aloes for a short time with nitric acid. (If the action be longer continued, the only products are aloetic and chrysammic acids.)

*Preparation.* 1. The alcoholic mother-liquor obtained in the preparation of aloetic acid ($C^{14}X^2H^4O^4$) is neutralised with chalk; the liquid filtered from the precipitate (containing oxalate of lime, &c.) is precipitated with neutral acetate of lead; and the precipitate is suspended in water, and decomposed by sulphuretted hydrogen: the liquid filtered from the sulphide of lead yields aloeretic acid by evaporation. (Mulder.)

—2. Crude chrysammic acid is boiled with carbonate of potash; the liquid filtered from the chrysammate of potash is precipitated by chloride of barium; and the precipitate decomposed by nitric acid. (Schunck.)

*Properties.* Brown amorphous mass. (Mulder.) When boiled with nitric acid, it is converted, first into aloetic, then into chrysammic acid. —With potash, soda, baryta and lime, it forms brown, soluble, uncrystallisable salts; with the oxides of lead and silver, it forms insoluble salts. (Mulder.) The lead-compound prepared in the manner above described contained in one preparation 63·0 p. c. (5 At.) of lead-oxide; in another, 58·24 p. c. (3 At.). The latter compound was converted into the former by boiling with water. The organic substance combined with the lead-oxide, gave the following composition:

| | | | Vlaanderen. |
|---|---|---|---|
| 14 C | 84 | 42·7 | 42·60 |
| N | 14 | 7·1 | 7·40 |
| H | 3 | 1·5 | 2·17 |
| 12 O | 96 | 48·7 | 47·83 |
| $C^{14}NH^3O^{12}$ | 197 | 100·0 | 100·00 |

## Aloetic Acid. $C^{14}N^3H^4O^{12}$. ?

E. Schunck. *Ann. Pharm.* 39, 24; 65, 235.
G. J. Mulder. *Scheik.* 5, 173; *J. pr Chem.* 48, 39.

*Formation.* By the continued action of nitric acid upon aloes, chrysammic acid being formed at the same time.

*Preparation.* 1. Crude chrysammic acid (p. 1), obtained by treating aloes with nitric-acid, is washed with water and boiled with alcohol, which dissolves the aloetic acid and leaves the greater part of the chrysammic acid. The chrysammic acid separates as the liquid cools; and the filtrate when evaporated yields aloetic acid still slightly contaminated with chrysammic acid, which separates on cooling from solution in boiling alcohol. The residual solution yields, by evaporation, pure crystalline aloetic acid. (The mother-liquor retains aloeretic acid.)

2. Crude chrysammic acid is boiled with carbonate of potash; the liquid filtered from the chrysammate of potash, which separates on cooling, is treated with chloride of barium; and the liquid filtered from the precipitated aloeretate of baryta (aloeretate and chrysatrate, according to Mulder) is mixed with nitric acid, which separates the aloetic acid. (Schunck.)

*Properties.* Orange-yellow crystalline powder. (Mulder.) Yellow amorphous powder. (Schunck.) Has a bitter taste and reddens litmus strongly.

| *Calculation, according to Schunck.* | | | | Found. |
|---|---|---|---|---|
| 16 C | 96 | 41·32 | | 40·75 |
| 2 N | 28 | 12·19 | | 11·59 |
| 4 H | 4 | 1·71 | | 1·73 |
| 13 O | 104 | 44·78 | | 45·93 |
| $C^{16}N^2H^4O^{13}$ | 232 | 100·00 | | 100·00 |

| *Calculation, according to Mulder.* | | | | Found. |
|---|---|---|---|---|
| 14 C | 84 | 41·4 | | 41·53 |
| 2 N | 28 | 13·8 | | 14·47 |
| 3 H | 3 | 1·5 | | 1·53 |
| 11 O | 88 | 43·3 | | 42·47 |
| $C^{14}N^2H^3O^{11}$ | 203 | 100·0 | | 100·00 |

| *Calculation.* | | | | Mean of the analyses by Schunck and Mulder. |
|---|---|---|---|---|
| 14 C | 84 | 39·6 | | 41·18 |
| 2 N | 28 | 13·2 | | 13·03 |
| 4 H | 4 | 1·8 | | 1·66 |
| 12 O | 96 | 45·4 | | 44·13 |
| $C^{14}N^2H^4O^{12}$ | 212 | 100·0 | | 100·00 |

Laurent (*Compt. Chim.* 1850, 165) assigns to aloetic acid the formula $C^{16}X^2H^4O^4$, which requires 42·86 per cent. of carbon. — According to the formula $C^{14}N^2H^4O^{12}$, aloetic acid is isomeric with binitrobenzoic acid $C^{14}X^2H^4,O^4$.

*Decompositions.* Aloetic acid treated with strong nitric acid, is completely converted into chrysammic acid, with evolution of hyponitric acid, but without formation of oxalic or picric acid. (Schunck):

$$C^{14}N^2H^4O^{12} + 2NO^5 = C^{14}N^2H^2O^{12} + 2HO + 2NO^4.$$

Protochloride of tin converts it into hydroaloetic acid. (Mulder.) When dry ammoniacal gas is passed over the acid, it takes fire even at 0°, giving off a large quantity of gas and forming a carbonaceous substance. (Mulder.)

*Combinations.* Aloetic acid dissolves sparingly in cold, more abundantly in boiling water. (Mulder.)

The aloetates are for the most part easily soluble in water.

*Aloetate of Potash.* — Small shining needles, which dissolve in water with blood-red colour, the solution when slowly evaporated depositing long ruby-coloured shining crystals. (Schunck.)

*Aloetate of Baryta.* — Obtained by heating aqueous aloetic acid with acetate of baryta. Brown-red nearly insoluble powder. (Mulder.)

| | | | | Mulder. |
|---|---|---|---|---|
| BaO | 76·6 | 27·39 | | 27·30 |
| 14 C | 84·0 | 30·04 | | 30·77 |
| 2 N | 28·0 | 10·01 | | 9·84 |
| 3 H | 3·0 | 1·07 | | 1·09 |
| 11 O | 88·0 | 31·49 | | 31·00 |
| $C^{14}N^2H^3BaO^{12}$ | 279·6 | 100·00 | | 100·00 |

*Aloetate of Lead.* — On mixing a solution of aloetate of baryta in a large quantity of water with neutral acetate of lead, a dark red powder is obtained insoluble in water. (Mulder.)

| | | | Mulder. |
|---|---|---|---|
| $C^{14}N^2H^8O^{11}$ | 203·0 | 47·6 | |
| 2 PbO | 223·6 | 52·4 | 54·5 |
| $PbO,C^{14}N^2H^3PbO^{12}$ | 426·6 | 100·0 | |

## Aloetamide.

$C^{14}N^3H^5O^{10} = C^{14}H^3AdX^2,O^2$.

MULDER. *Scheik.* 5, 178; abstr. *J. pr. Chem.* 48, 9.

*Formation.* By the action of dilute ammoniacal gas on aloetic acid. — The acid dissolves in aqueous ammonia, forming a solution of a beautiful violet colour.

*Preparation.* Ammoniacal gas, largely diluted with air is passed over dry aloetic acid; the acid then loses water and assumes a deep violet colour.

*Properties.* Aloetamide is much darker in colour and much more soluble than chrysammide.

| | | | Mulder. |
|---|---|---|---|
| 14 C | 84 | 39·81 | 39·16 |
| 3 N | 42 | 19·90 | 20·58 |
| 5 H | 5 | 2·37 | 2·54 |
| 10 O | 80 | 37·92 | 37·72 |
| $C^{14}N^3H^5O^{10}$ | 211 | 100·00 | 100·00 |

*Decompositions.* Nitric acid converts the compound immediately into aloetic acid and nitrate of ammonia. Heated with hydrochloric acid, it yields sal-ammoniac and aloetic acid. The aloetic acid thus obtained has a green colour.

## Chrysatric Acid.

SCHUNCK. *Ann. Pharm.* 55, 240.
MULDER. *Scheik.* 5, 194; abstr. *J. pr. Chem.* 48, 16.

Produced by the action of alkalies, caustic baryta, or lime, on chrysammic acid. Was regarded by Schunck (*Ann. Pharm.* 65, 234) as aloeretic acid.

Chrysammic acid heated with potash-ley is dissolved, forming a dark brown liquid from which acetic acid expels carbonic and formic acids,

but does not precipitate any thing. When strong potash-solution is used, ammonia is given off, and on addition of an acid, hydrocyanic acid [?] escapes. — When chrysammic acid is heated with moderately strong solution of potash, till the whole is dissolved, the addition of acetate of lead to the cooled liquid gives rise to a brown precipitate of chrysatrate of lead. (Mulder.)

| | | | | Rost van Tonningen, *at* 150°. |
|---|---|---|---|---|
| 4 PbO | 447·2 | | 58·90 | 58·71 |
| 24 C | 144·0 | | 18·96 | 19·08 |
| 3 N | 42·0 | | 5·53 | 5·51 |
| 6 H | 6·0 | | 0·79 | 0·78 |
| 15 O | 120·0 | | 15·82 | 15·92 |
| | 759·2 | | 100·00 | 100·00 |

From another preparation 55·03 p. c. of lead oxide was obtained; but the organic substance united with it had the same composition. (Mulder.)

According to Schunck, the solution of chrysammate of potash is precipitated by acids; the resulting brown precipitate he names aloeretic acid. When the solution is precipitated by chloride of barium, and the washed precipitate treated with a small quantity of sulphuric acid, a liquid is obtained which contains baryta and when evaporated leaves a residue of delicate laminæ containing:

| | | | | Schunck. |
|---|---|---|---|---|
| BaO | 76·6 | | 30·27 | 30·80 |
| 12 C | 72·0 | | 28·47 | 28·03 |
| 2 N | 28·0 | | 11·22 | |
| 4 H | 4·0 | | 1·58 | 1·82 |
| 9 O | 72·0 | | 28·46 | |
| | 252·6 | | 100·00 | |

## Chryiodin.

MULDER. *Scheik.* 5, 209; abstr. *J. pr. Chem.* 48, 19.

Chrysammic acid boiled with oil of vitriol, is converted, with very violent evolution of hyponitric acid, sulphurous acid, carbonic oxide, and carbonic acid, into a dark violet substance which Mulder calls chryiodin.

| | *Calculation.* | Mulder. |
|---|---|---|
| 56 C | 55·1 | 55·50 |
| 3 N | 6·9 | 6·35 |
| 8 H | 1·3 | 1·90 |
| 28 O | 36·7 | 36·25 |
| $C^{56}N^{3}H^{8}O^{28}$ | 100·0 | 100·00 |

Chryiodin heated with strong nitric acid, yields a large quantity of hyponitric acid vapours, and a red solution, which does not contain

chrysammic acid. It dissolves in dilute potash-ley, forming a beautiful violet-coloured liquid from which it is again separated as a violet-coloured jelly by hydrochloric acid.

Chryiodin is but partially soluble in ammonia; the undissolved portion, after being washed with water, forms a blue jelly of *chryiodamide.*

| | *Calculation.* | Rost Van Tonningen, *at* 120°. |
|---|---|---|
| 28 C | 52·4 | 52·45 |
| 3 N | 13·0 | 14·03 |
| 8 H | 2·5 | 2·81 |
| 13 O | 32·1 | 30·71 |
| $C^{28}N^{3}H^{8}O^{13}$ | 100·0 | 100·00 |

The portion dissolved in ammonia yields by evaporation, indigo-coloured *chryiodide of ammonium* insoluble in pure water.

| | *Calculation.* | Mulder, *at* 120°. |
|---|---|---|
| 28 C | 49·8 | 50·1 |
| 4 N | 16·5 | 16·4 |
| 10 H | 2·9 | 3·2 |
| 13 O | 30·8 | 30·3 |
| $C^{28}N^{4}H^{10}O^{13}$ | 100·0 | 100·0 |

This compound dissolves readily, with evolution of ammonia, in caustic potash, forming a violet solution which is precipitated by hydrochloric acid. When heated with hydrochloric acid, it yields ammonia, the colour of the warm solution becoming lighter.

## Hydrochrysammide.

E. Schunck. *Ann. Pharm.* 65, 241.

Produced by the action of reducing agents on chrysammic or aloetic acid.

1. When chrysammic acid is introduced into a boiling solution of sulphide of potassium containing excess of potash, it dissolves with deep blue colour, and the solution, on cooling, deposits a large quantity of needle-shaped crystals which are recrystallised from boiling potash-ley, and then washed and dried.

2. Chrysammic acid is boiled with an aqueous solution of protochloride of tin, whereupon the liquid immediately turns blue, and after the excess of acid and of tin-salt has been removed, and the residue dissolved in boiling potash-ley, the hydrochrysammide crystallises out on cooling, but is difficult to free from oxide of tin.

Indigo-coloured, nearly black needles, copper-coloured by reflected light, and having a metallic lustre. — When heated in a tube, they give

off violet vapours which deposit blue crystals on the cold parts of the tube; but the greater part of the substance is decomposed, with evolution of ammonia.

| | | | Schunck. |
|---|---|---|---|
| 14 C | 84 | 50·60 | 50·64 |
| 2 N | 28 | 16·86 | 15·32 |
| 6 H | 6 | 3·61 | 3·52 |
| 6 O | 48 | 28·93 | 30·52 |
| $C^{14}N^2H^6O^6$ | 166 | 100·00 | 100·00 |

[According to this, the substance is isomeric with nitrobenzamide = $C^{14}XAdH^2,O^2$; but as it decomposes without detonation when heated, it does not appear to contain hyponitric acid, and is perhaps $C^{14}Ad^2H^2O^6$ (= $C^{14}Ad^2H^2O^4,O^2$ ?). L.].

When heated on platinum foil, it decomposes without detonation.—Boiled with nitric acid, it gives off a large quantity of red fumes, and yields a dark brown liquid not containing chrysammic acid.—When suspended in water through which chlorine gas is passed, it is gradually decomposed and dissolved.

It is insoluble in water, but dissolves with brown colour in oil of vitriol, whence it is precipitated in small flakes by water. It dissolves in caustic and in carbonated alkalies, forming indigo-coloured solutions, whence it is precipitated in blue flakes by acids.

In boiling *alcohol*, it dissolves sparingly, with faint blue colour.

Mulder (*Scheik.* 5, 208), by heating chrysammic acid with ammonia and passing sulphuretted hydrogen into the warm liquid, obtained a blue liquid and a blue substance which remained undissolved: this latter he designated as *chrysindide of oxide of ammonium.*

The blue liquid yielded by evaporation a blue residue, called by Mulder *chrysindamide.* Both these bodies contained sulphur mechanically mixed, and were otherwise constituted as follows:

*Chrysindide of Oxide of Ammonium.*

| | Calculation. | Mulder. |
|---|---|---|
| 28 C | 48·0 | 47·5 |
| 5 N | 20·0 | 20·1 |
| 8 H | 2·3 | 2·5 |
| 13 O | 29·7 | 29·9 |
| | 100·0 | 100·0 |

*Chrysindamide.*

| | Calculation. | Mulder. |
|---|---|---|
| 28 C | 43·0 | 43·4 |
| 5 N | 17·9 | 17·5 |
| 9 H | 2·4 | 2·7 |
| 18 O | 36·7 | 36·4 |
| | 100·0 | 100·0 |

By boiling chrysammic or aloetic acid with excess of protochloride of tin, Mulder (*Scheik.* 5, 181; *J. pr. Chem.* 48, 12) obtained a black-violet powder consisting of *hydroaloetate of stannic oxide.*

| | | Mulder. |
|---|---|---|
| 3 $SnO^2$ | 52·4 | 52·0 |
| 14 C | 19·5 | 19·3 |
| 2 N | 6·6 | 6·4 |
| 4 H | 0·9 | 1·1 |
| 11 O | 20·6 | 21·2 |
| | 100·0 | 100·0 |

This compound, when immersed in potash-ley, gives off ammonia, and assumes a fine blue colour; heated with nitric acid, it deposits binoxide of tin, and forms a red solution with evolution of nitrous fumes. In this reaction, aloetic acid is first formed and afterwards chrysammic acid. (Mulder.)

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## BENZYLENE SERIES.

### A. Primary Series.

### Primary Nucleus $C^{14}H^{6}$.

¶. A resinous body having this composition is produced by the action of fluoride of boron on benzylic alcohol. It gave by analysis 92·86 p. c. carbon and 6·82 p. c. hydrogen, the formula requiring 93·33 C and 6·67 H; but the physical properties of the body show that it is rather polymeric with benzylene, probably stilbene $C^{28}H^{12}$. A resinous substance having the same properties and probably also the same composition is obtained by the action of oil of vitriol, chloride of zinc, anhydrous phosphoric acid or anhydrous boracic acid on benzylic alcohol or benzylic ether. (Cannizzaro, *Ann. Pharm.* 92, 113.)

### ¶. Benzylic Ether.

$C^{14}H^{7}O = C^{14}H^{6},HO$.

Cannizzaro. *Ann. Pharm.* 92, 115.

*Formation and Preparation.* By the action of anhydrous boracic acid on benzylic alcohol. Fused and pulverised boracic acid is mixed up to a paste with benzylic alcohol; the mixture heated for some hours to between 120° and 125° in a closed flask placed in an oil-bath; and the resulting hard brown mass, treated with boiling water and solution of an alkaline carbonate to remove the boracic acid. A greenish brown oil then rises to the surface; and on subjecting this oil to distillation, unaltered benzylic alcohol passes over below 300°, and benzylic ether between 300° and 315°. In the retort there remains a quantity of the resinous hydrocarbon above mentioned ($C^{14}H^{6}$ or $C^{28}H^{12}$) saturated with benzylic ether, which cannot be separated from the resin by distillation, because it decomposes at the temperature required to effect the separation.

*Properties.* Colourless, oily liquid, exhibiting when viewed in certain directions, a slight indigo tint. This colour likewise shows itself on the edges of

the resinous hydrocarbon when it is saturated with the ether. Boils between 300° and 315°.

| | | | | Cannizzaro (*mean*). |
|---|---|---|---|---|
| 14 C | 84 | | 84·85 | 84·51 |
| 7 H | 7 | | 7·07 | 7·28 |
| O | 8 | | 8·08 | 8·21 |
| $C^{14}H^7O$ | 99 | | 100·00 | 100·00 |

May also be regarded as $C^{28}H^{14}O^2 = \left.\begin{matrix}C^{14}H^7\\C^{14}H^7\end{matrix}\right\}O^2$.

*Decompositions.* 1. The ether heated in a sealed tube, a few degrees above 315°, assumes an amber colour and is decomposed, yielding a very small quantity of the resinous hydrocarbon, bitter almond oil (which may be extracted by means of bisulphite of soda), and a light oil which has the odour of toluol, $C^{14}H^8$, and, like that body, does not solidify in a freezing mixture. Probably, a portion of the ether is resolved into water and the resinous hydrocarbon:

$$C^{28}H^{14}O^2 = 2HO + C^{28}H^{12};$$

and the rest into bitter almond oil and toluol:

$$C^{28}H^{14}O^2 = C^{14}H^6O^2 + C^{14}H^8.$$

No gaseous product is evolved.—2. The ether heated with oil of vitriol or anhydrous phosphoric acid is converted into a resinous substance, which appears to be identical with that which is obtained by the same means from benzylic alcohol. (Cannizzaro.)

## ¶. Ethylo-benzylic Ether.

$$C^{18}H^{12}O^2 = C^4H^5O,C^{14}H^7O.$$

CANNIZZARO. *Il nuovo Cimento.* 3, 397; Liebig & Kopp's *Jahresbericht*, 1856, 581.

*Vinobenzylic ether, Benzylovinic ether, Benzylate of ethyl, Ethylate of benzyl.*

Obtained by the action of chloride of benzyl on ethylate of potassium:

$$C^{14}H^7Cl + C^4H^5KO^2 = KCl + C^{18}H^{12}O^2.$$

Chloride of benzyl is boiled with an alcoholic solution of potash in an apparatus in which the condensed vapours can continually flow back; and the resulting liquid is decanted from the chloride of potassium, and mixed with water, whereupon it separates into two layers, the lower of which is a concentrated solution of potash, and the upper, ethylo-benzylic ether. The latter is distilled, and the portion which passes over at 185°, is dried by contact with chloride of calcium and rectified.

Colourless, mobile liquid, specifically lighter than water, and having an agreeable odour. Boils at 185°. Insoluble in water. ¶.

## Benzylic Alcohol.

$C^{14}H^{8}O^{2} = C^{14}H^{6},H^{2}O^{2}$.

CANNIZZARO. (1853). *Ann. Pharm.* 88, 129; 90, 252; 92, 113; 96, 246. — More fully: *Il nuovo Cimento*, 1, 84; 2, 212; 3, 397.

***Benzoic alcohol, Benzalkohol, Benzalalkohol, Benzoesäure-alkohol.***

*Formation and Preparation.* — 1. When a solution of 1 vol. perfectly purified bitter almond oil in 3 vol. alcohol is mixed with 5 or 6 vol. of a saturated alcoholic solution of potash, the mixture becomes heated, and is converted into a crystalline magma, consisting of benzoate of potash mixed with alcoholic potash and benzylic alcohol:

$$\underbrace{2C^{14}H^{6}O^{2}}_{\text{bitter almond oil.}} + KO,HO = \underbrace{C^{14}H^{5}KO^{4}}_{\text{benzoate of potash.}} + \underbrace{C^{14}H^{8}O^{2}}_{\text{benzylic alcohol.}}.$$

The benzoate of potash is dissolved out by hot water; the alcohol distilled off; water added to the residue till the liquid begins to show turbidity; the liquid then shaken up with ether, which dissolves the benzylic alcohol; the ether expelled from the solution by the heat of the water-bath; the brown oily residue distilled; and the distillate rectified, after having been dehydrated by fused potash. — 2. When acetate of benzyl obtained by boiling chloride of benzyl or chlorotoluol with concentrated alcoholic potash, is boiled for a considerable time with a strong alcoholic solution of potash, and the greater part of the vinic alcohol distilled off, the residual liquid separates into two layers, the uppermost of which contains benzylic alcohol. By rectifying this liquid and collecting apart the portion which goes over at 204°, benzylic alcohol is obtained in the pure state.

*Properties.* Colourless, strongly refracting oily liquid, having a faint agreeable odour. Sp. gr. 1·089 (Cannizzaro); 1·0507 at 14·4° or 1·0628 at 0° (H. Kopp, *Ann. Pharm.* 94, 313); boiling point 204° (Cannizzaro); 206·5° at 751·4 mm. (Kopp.) Vapour-density between 3·84 and 3·85. (Cannizzaro.)

*Calculation.*

| | | |
|---|---|---|
| 14 C | 84 | 77·77 |
| 8 H | 8 | 7·41 |
| 2 O | 16 | 14·82 |
| $C^{14}H^{8}O^{2}$ | 108 | 100·00 |

| | Vol. | Density. |
|---|---|---|
| C-vapour | 14 | 5·8240 |
| H-gas | 8 | 0·4874 |
| O-gas | 1 | 1·1093 |
| Alcohol-vapour | 2 | 7·4207 |
| | 1 | 3·7103 |

*Decompositions.* 1. The vapour passed through a red-hot tube filled with spongy platinum, yields an oil which floats on water, and is a mixture of benzol ($C^{12}H^6$), a volatile solid body, and other compounds not yet examined. — 2. A solution of benzylic alcohol in bisulphide of carbon forms with iodide of phosphorus, a liquid which attacks the eyes strongly, and appears to be hydriodate of benzylene, or iodide of benzyl, $C^{14}H^7I$; with larger quantities of iodide of phosphorus, a crystalline compound, $C^{14}H^8O^3$ is obtained. Cannizzaro found 72·36 p. c. C and 6·53 H, while the formula requires 72·41 C and 6·89 H.—3. When hydrochloric acid gas is passed into benzylic alcohol, the liquid becomes heated, and hydrochlorate of benzylene or chloride of benzyl $C^{14}H^7Cl$ is formed. — 4. When benzylic alcohol is heated with 2 or 3 vol. of strong *nitric acid*, a violent action takes place, continuing after the mixture has been removed from the fire; bitter almond oil is produced and rises to the surface of the liquid. — 5. Aqueous *chromic acid* converts benzylic alcohol into benzoic acid. — 6. *Oil of vitriol* produces a resin insoluble in water, alcohol and ether, sparingly soluble in Nordhausen sulphuric acid, and becoming somewhat soft when immersed in warm water. — 7. The alcohol heated with anhydrous *phosphoric acid* or with *chloride of zinc*, yields a resin similar to that which is produced by the action of oil of vitriol. — 8. Fused *boracic acid* between 100° and 120° converts benzylic alcohol into benzylic ether $C^{14}H^7O$ [or $C^{28}H^{14}O^2$]; but at higher temperatures this ether is converted into benzylene $C^{14}H^6$ [or stilbene $C^{28}H^{12}$] (p. 16). The same products are probably formed by the action of oil of vitriol, anhydrous phosphoric acid, and chloride of zinc. — 9. Fluoride of boron acts energetically and with evolution of heat, upon benzylic alcohol, forming boracic acid, hydrofluate of boracic acid, and benzylene $C^{14}H^6$ [or stilbene]. Fluoride of silicium has no action upon benzylic alcohol.

10. When 1 vol. benzylic alcohol is distilled with 4 or 5 vol. of a saturated alcoholic solution of potash in an apparatus in which the less volatile products can flow back, there passes over, after the mixture has become solid, a very mobile liquid, which is lighter than water, resembles benzol, and consists of a mixture of unaltered benzylic alcohol, and a fluid hydrocarbon which boils at 114°, and has the odour and composition of toluol. Cannizzaro remarks that this oil is related to the benzylene series in the same manner as marsh gas to the methylene series. Should this supposed identity with toluol be established, the latter must take its place in the benzylene series.

*Combinations.* Benzylic alcohol mixes in all proportions with *bisulphide of carbon, alcohol, ether* and *acetic acid.*

## Bitter Almond Oil.

$C^{14}H^6O^2 = C^{14}H^6,O^2$.

MARTRÈS. *J. Pharm.* 5, 289.
A. VOGEL. *Schw.* 20, 66; 32, 119.
SCHRADER. *Berl. Jahrb.* 1826; 2, 43.
ROBIQUET. *Ann. Chim. Phys.* 15, 29. — *J. Pharm.* 8, 295; also *Ann. Chim. Phys.* 21, 250.
STANGE. *Repert.* 14, 329 and 361; 16, 80.

ROBIQUET and BOUTRON CHARLARD. *Ann. Chim. Phys.* 44, 352; also *Pogg.* 20, 494.
WÖHLER & LIEBIG. *Ann. Pharm.* 22, 1; also *Pogg.* 26, 328.
WINCKLER. *Repert.* 53, 289; 92, 328. — *Jahrb. pr. Pharm.* 22, 89.
LAURENT. *Ann. Chim. Phys.* 62, 25; 65, 192; 66, 181; 69, 397. — *N. Ann. Chim. Phys.* 1, 292; 36, 342. — *Inst.* 1840, 362. — *Rev. scient.* 18, 200.
ZININ. *Ann. Pharm.* 34, 188.
ROCHLEDER. *Ann. Pharm.* 37, 346.
VOLCKEL. *Pogg.* 62, 444.
LEPAGE. *J. Chim. méd.* 24, 365; abstr. *N. J. Pharm.* 15, 40. — *N. J. Pharm.* 15, 274.
GREGORY. *Ann. Pharm.* 54, 372.
QUADRAT. *Ann. Pharm.* 71, 13.
BERTAGNINI. *Ann. Pharm.* 79, 259; 85, 183.

*Benzaldide, Laurel oil, Kirschlorbeeröl, Peach-leaf oil, Pfirsichblätteröl, Traubenkirschenöl, Hydride of Benzoyl, Oxide of Picramyl, Essence d'amandes amères.*

Martrès (1803), Vogel and Schrader found that almonds may be made to yield, in addition to fixed oil and prussic acid, a peculiar volatile oil; Stange showed that the crystallised acid produced from bitter almond oil is benzoic acid; Robiquet, Wöhler & Liebig demonstrated the mode of formation of bitter almond oil; and Wöhler & Liebig, in 1832, determined its composition and described its properties.

The amygdaliferous parts of Pomeæ, Amygdaleæ, and shrubby Spireæ, when macerated in cold water and distilled, yield, after a while, bitter almond oil and hydrocyanic acid. (*Comp.* vii, 389; also Wicke, *Ann. Pharm.* 79, 79; 81, 241; 83, 176.) — This volatile oil does not exist ready formed in the dry tissues of the plants; for the oil expressed from dry bitter almonds has neither smell nor taste (Martrès, Robiquet); and no volatile oil is extracted by alcohol or ether from bruised bitter almonds (Robiquet & Boutron Charlard), from dry laurel leaves, (Winckler, Lepage), or from the bark of *Prunus padus.* (Winckler.) Laurel leaves treated with boiling water and distilled yield little or no bitter almond oil. (Winckler, Lepage.) — Fresh laurel leaves contain a small quantity—proportional to their amount of water—of bitter almond oil and hydrocyanic acid, which may be extracted by ether (Winckler, Lepage); also the leaves of *Prunus padus* and *Amygdalus persica.* (Winckler.)

*Formation.* 1. By heating benzylic alcohol with strong nitric acid. (Cannizzaro, *Ann. Pharm.* 88, 180.) — 2. By the action of hydride of copper on chloride of benzoyl. (Chiozza, *Compt. rend.* 36, 631.) — 3. By the dry distillation of sugar. (Völckel, *Ann. Pharm.* 85, 68.) — Furfurol obtained by the dry distillation of sugar, appears by its odour to contain traces of bitter almond oil. (Völckel.) — 4. By the action of nascent hydrogen, evolved by the action of zinc or hydrochloric acid, upon cyanide of benzoyl (*q. v.*) hydrocyanic acid being formed at the same time. The same transformation is effected, though less quickly, by heating the cyanide of benzoyl with mercury and hydrochloric acid. (Kolbe, *Ann. Pharm.* 98, 344.) — 5. By the action of nitric acid upon oil of cinnamon. (Mulder, *J. pr. Chem.* 18, 385.) By heating cinnamic acid

with nitric acid or peroxide of lead. (Dumas & Peligot, Mulder, Mitscherlich.) — 6. By boiling styracin or styrone with sulphuric acid and peroxide of manganese (Joel, *Ann. Pharm.* 70, 5), or styracin with aqueous chromic acid. (Laurent.) — 7. By heating stilbene with aqueous chromic acid. (Laurent.) — 8. By boiling protein-substances with aqueous chromic acid or with sulphuric acid and peroxide of manganese. (Guckelberger, *Ann. Pharm.* 64, 39; Keller, *Ann. Pharm.* 72, 26). — 9. By the decomposition of mandelic acid. — 10. By the decomposition of amygdalin. — 11. By subjecting a mixture of benzoate and formiate of lime, in successive small portions, to rapid dry distillation:

$$\underbrace{(C^{14}H^5O^2,O)CaO}_{\text{benzoate of lime.}} + \underbrace{C^2HO^3,CaO}_{\text{formiate of lime.}} = \underbrace{C^{14}H^5O^2,H}_{\text{bitter almond oil.}} + 2(CaO,CO^2).$$

A brown oily liquid then passes over, from which the bitter almond oil may be separated by combination with bisulphite of soda. (Piria, *Cimento*, 3, 126; *Ann. Pharm.* c. 104; see also Limpricht, *Ann. Pharm.* 97, 368.

*Preparation.* Bitter almonds freed from fixed oil by cold pressing, are stirred up to a thin paste with water, the mixture left to stand for between 12 and 24 hours at the ordinary temperature (between 30° and 40°, according to Bolle, *N. Br. Arch*, 37, 30) and then distilled with water.

If the distillation is performed over the open fire, the mass is very apt to froth over, especially, at the beginning of the ebullition, when the emulsion coagulates, and forms capsular envelopes round the vapour-bubbles. It is necessary therefore to use a capacious vessel, and to keep the heat moderate at the beginning, or else to break the bubbles by stirring. Haenle, after macerating the almond-paste to a pulp, throws it into the still when the water is already boiling. (*Repert.* 18, 383.) — But the surest way of preventing the mass from boiling over, as well as from burning, is to distil it by a steam-heat, either by placing the almond-paste (mixed with chopped straw, according to Heussler, *Jahrb. pr. Pharm.* 7, 367), on a cloth resting on the flat sieve-formed bottom of the still, and passing steam through it, or by covering the bottom of an ordinary still with a layer of coarse sand several inches thick, and saturated with water (Veling), or again by covering the bottom of the still with a moderately thick layer of straw, pouring water upon this, then covering it with a coarse cloth, and pouring the almond-paste upon the cloth. (Mohr.) Another method is to strain through a cloth the liquid obtained by macerating the almonds for 24 hours, press the residue, again stir it up with water, and strain, and lastly subject to distillation the liquid thus freed from the greater portion of the solid matter. (Wöhler, *Handwörterbuch*, 1, 747.)

The heavy oil which passes over contains prussic acid and various products of decomposition (according to Henry & Plisson, *J. Pharm.* 14, 451, it consists of 74·40 p. c. C, 5·84 H, 5·9 N and 11·79 O), and therefore requires purification. This is effected: (*a*). By repeated agitation with potash-ley (1 pt. hydrate of potash to 1 pt. water), (A. Vogel, Schrader,) or with ferrous or ferroso-ferric hydrate (obtained by mixing an aqueous solution of green vitriol or protochloride of iron with potash or hydrate of lime (Schrader, Wöhler & Liebig, Winckler), or with

water and a small quantity of mercuric oxide (v. Ittner), and distilling. — (*b*). Or by agitating the oil with three or four times its volume of an aqueous solution of bisulphite of soda, of 27° B.; collecting on a filter the crystalline mass which forms after some hours; leaving it to dry on a porous tile; washing with cold alcohol; then dissolving in the smallest quantity of cold water; and decomposing the solution with carbonate of soda. The oil which rises to the top of the liquid is then decanted and distilled with chloride of calcium. (Bertagnini.)

A quantity of bitter almond oil which had acquired a yellow colour from the burning of the paste, became in the course of five months, black-brown and opaque. Cotton was soaked in the oil and the liquid distilled; a colourless oil then passed over, the colouring matter remaining attached to the cotton. (Schlesinger, *Repert.* 22, 145.) — [Respecting the preparation and purification of bitter almond oil, see also G. Whipple, *Pharm. J. Trans.* 13, 597; and Groves, *ibid.* 599.]

¶ 2. *From Cyanide of Benzoyl.* — Hydrochloric acid is poured upon cyanide of benzoyl in a tubulated retort; heat applied sufficient to melt the crystallised cyanide; and granulated zinc introduced. The evolution of hydrogen caused by the action of the zinc on the hydrochloric acid, ceases as soon as the vessel is shaken so as to bring the cyanide of benzoyl well in contact with the zinc, the hydrogen, as it is evolved, then combining, partly with the cyanogen and partly with the benzoyl to form bitter almond oil $C^{14}H^{6}O^{2},H$; after a while, the liquid cyanide in contact with the zinc acquires a yellow colour, the odour of hydrocyanic acid becomes apparent, and afterwards that of bitter almond oil. A considerable quantity of zinc is required to render the transformation complete. Towards the end of the operation, the zinc becomes covered with a dirty yellow unctuous mass, which when heated with excess of potash-ley, is decomposed, with formation of yellowish red oily drops; and on subsequently distilling the liquid, bitter-almond oil passes over in considerable quantity [and may be further purified by means of bisulphite of soda in the manner above described]. (Kolbe.) — At a later period of the distillation, the distillate becomes milky and contains benzoïn, a body polymeric with bitter almond oil. To prevent this conversion of the bitter almond oil into benzoïn, a portion of the yellow unctuous mass was distilled with milk of lime, after addition of protosulphate of iron; the distillate however contained only traces of bitter almond oil: hence Kolbe concludes that the yellow mass contains bitter almond oil, not merely in a state of mixture, but chemically combined with some other substance (perhaps with hydrocyanic acid as described by Völkel, *Pogg.* 62, 444), forming a compound which is decomposed by hot potash-ley, but not by hydrate of lime. ¶

*Properties.* Colourless, mobile, strongly refracting liquid. Sp.gr. 1·043 (Wöhler & Liebig); 1·075 (Chardin Hadancourt; 1·0499 at 14·6° or 1·0636 at 0° (H. Kopp, *Ann. Pharm.* 94, 314); boils at 180°; (according to Kopp, its boiling point is 179·1°, when the barometer stands at 751·3 mm.) — It has a peculiar odour and burning aromatic taste. When perfectly free from hydrocyanic acid, it exerts merely a stimulating not a poisonous action. (Robiquet, Grindley, *Repert.* 97, 222; Wöhler & Frerichs, *Ann. Pharm.* 66, 336.)

| | | | | Wöhler & Liebig. | Guckelberger *from casein.* | Kolbe *from cyanide of benzoyl.* |
|---|---|---|---|---|---|---|
| 14 C | 84 | 79·24 | 79·520 | 79·11 | 79·2 |
| 6 H | 6 | 5·65 | 5·715 | 5·80 | 5·7 |
| 2 O | 16 | 15·11 | 14·738 | 15·09 | 15·1 |
| $C^{14}H^{6}O^{2}$ | 106 | 100·00 | 100·000 | 100·00 | 100·0 |

The radical theory assumes the existence of a radical, *Benzoyl* = Bz; and if, as assumed by Wöhler & Liebig, this radical = $C^{14}H^5O^2$, then bitter almond oil is the hydride of benzoyl = BzH, and hypothetical anhydrous benzoic acid is BzO, or if, according to the hypothesis of Berzelius, Bz = $C^{14}H^5$, then bitter almond oil is BzO,HO, and hypothetical anhydrous benzoic acid is $BzO^3$. Laurent assumes the existence of a radical called *picramyl*, Pcr = $C^{14}H^6$, the oxide of which is bitter almond oil = $PcrO^2$. — As bitter almond oil treated with alcoholic potash yields benzylic alcohol and benzoic acid, List & Limpricht (*Ann. Pharm.* 90, 190) suppose that it is analogous in composition to the compound ethers, and to be regarded as $C^{14}H^7O,C^{14}H^5O^3$; but since Cannizzaro has actually formed the benzoate of benzyl, and shown that it possesses totally different properties, it is best for the present, to regard bitter almond oil as the aldehyde of the benzylene series.

*Decompositions.* 1. The vapour is not decomposed by merely passing through a *red-hot tube* (Wöhler and Liebig), but when slowly passed through a red-hot tube filled with fragments of pumice-stone, it is resolved into benzol and carbonic oxide gas. (Barreswil and Boudalt, *N. J. Pharm.* 5, 265):

$$C^{14}H^6O^2 = C^{12}H^6 + 2CO.$$

2. Bitter almond oil, in contact with oxygen gas either dry or moist, or with the air, absorbs oxygen, and is converted into benzoic acid (A. Vogel, Stange, Robiquet, Stenhouse, *Ann. Pharm.* 89, 253), without the simultaneous formation of any other products. (Wöhler and Liebig.) The action is accelerated by heat (Stange) or by sunshine. (Wöhler & Liebig.) It burns with a luminous and very sooty flame. (A. Vogel, Wöhler & Liebig.)

4. By dry *chlorine*, it is converted into chloride of benzoyl and hydrochloric acid; by bromine into bromide of benzoyl and hydrobromic acid. (Wöhler & Liebig):

$$C^{14}H^6O^2 + 2Cl = C^{14}H^5ClO^2 + HCl.$$

When chlorine gas is passed for several days into bitter almond oil, and the liquid ultimately warmed, there is obtained a crystalline mixture of benzoic acid, chloride of benzoyl, and stilbesous acid. (Laurent.) In moist chlorine gas, bitter almond oil immediately becomes white and crystalline (A. Vogel); when saturated with moist chlorine gas, it yields benzoate of bitter almond oil, and hydrochloric acid. (Robiquet & B. Charlard, Liebig, Laurent.) — 5 In cold strong *nitric acid*, bitter-almond oil dissolves without decomposition (Liebig & Wöhler); by fuming nitric acid or by a mixture of nitric acid and oil of vitriol, it is converted into hydride of nitrobenzoyl. (Bertagnini.) — By continued boiling with aqueous *iodic acid*, bitter-almond oil is converted into benzoic acid, without any formation of carbonic acid. (Müller, *Compt. rend.* 19, 271.) — 7. It dissolves in cold *oil of vitriol* without decomposition; the solution when heated, becomes purple-red, and then black, with evolution of carbonic acid. — When 1 pt. of fuming sulphuric acid is poured upon 3 pts. of bitter-almond oil, the liquid becomes heated, turns brown and thick, and on cooling forms a solid mixture of unaltered bitter almond oil and stilbylous acid. (Laurent.) With anhydrous sulphuric acid, bitter almond oil forms sulphomandelic acid. (Mitscherlich, *Lehrb.* Aufl. 4, 1, 163.)

8. Bitter-almond oil heated with *pentachloride of phosphorus*, forms chloride of benzylene and oxychloride of phosphorus (Cahours, *Compt. rend.* 25, 725):

$$C^{14}H^6O^2 + PCl^5 = C^{14}H^6Cl^2 + PCl^3O^2.$$

9. With *chloride of sulphur*, bitter-almond oil becomes somewhat strongly

heated, and the liquid on cooling yields crystals of stilbylous acid. (Laurent.)

10. Bitter almond water containing hydrocyanic acid, evaporated with *hydrochloric acid* at a temperature below 100°, yields hydrocyanate of bitter almond oil. (Vogel, *Pogg.* 62, 444.) On boiling the liquid, mandelic acid is produced. (Winckler, Liebig, *Ann. Pharm.* 18, 310.)

11. Bitter almond oil in contact with *aqueous potash*, is converted in a few weeks into benzoin. (Robiquet, Wöhler & Liebig, Laurent.) This transformation is very much accelerated by the presence of cyanide of potassium. — Bitter almond oil which has not been rectified, and therefore contains prussic acid, when shaken up with dilute potash and alcohol, is converted in the course of 24 hours into benzoin. The oil frequently remains liquid after 48 hours, but if then agitated, it solidifies in a few minutes. (Laurent. *Ann. Chim. Phys.* 66, 193.) — When bitter almond oil containing prussic acid, is dissolved in hot alcoholic potash, it solidifies after a few minutes, into a yellow crystalline mass consisting of benzoin slightly contaminated with resin. (Zinin, *Ann. Pharm.* 34, 186.) — When either pure or commercial bitter almond oil is mixed with $\frac{1}{4}$ of its volume of nearly anhydrous prussic acid, and the mixture shaken up with alcoholic potash, there is formed, after a while, a flocculent precipitate consisting of $C^{42}H^{18}Cy^{2}O^{4}$. Pure bitter almond oil is converted into benzoin with nearly equal facility by contact with a weak alcoholic solution of cyanide of potassium. (Zinin, *Ann. Pharm.* 34, 188.) Gregory obtained the same body by leaving commercial bitter almond oil for ten years in contact with strong potash-ley. (*Ann. Pharm.* 54, 371.) — When bitter almond oil is heated with solid *hydrate of potash*, hydrogen gas is evolved and benzoate of potash formed. (Wöhler & Liebig.) — In alcoholic potash, even out of contact with the air, bitter almond oil forms benzoate of potash, without evolution of hydrogen. (Liebig & Wöhler.) By the action of alcoholic potash upon bitter almond oil, benzylic alcohol is produced. (Cannizzaro, *Ann. Pharm.* 88, 129.) When bitter almond oil is heated with alcoholic potash, benzoate of potash is formed, together with an oily liquid which appears to be benzylic alcohol. (List & Limpricht, *Ann. Pharm.* 90, 190.)

12. With *ammonia*, bitter almond oil forms a crystalline mass consisting principally of hydrobenzamide, $C^{24}N^{2}H^{18}$. — Rectified bitter almond oil which had passed over at 180°, was covered with aqueous ammonia, and left to stand without agitation for 8 days; $\frac{9}{10}$ of the oil was then converted into a solid crystalline mass consisting of nearly pure hydrobenzamide. (Laurent, *Ann. Chim. Phys.* 62, 24.) — Bitter almond oil set aside for some days in contact with saturated aqueous ammonia, is converted slowly but completely into hydrobenzamide. (Fownes, *Ann. Pharm.* 54, 363.) — Bitter almond oil immersed in aqueous ammonia and left to itself in a closed vessel, is converted, in 24—48 hours at ordinary temperatures, or in 6—8 hours when heated to the boiling point of the aqueous ammonia, into a yellow resinous mass, $\frac{9}{10}$ of which consists of hydrobenzamide, and the remaining $\frac{1}{10}$ of a yellowish green viscid resin having a disagreeable odour. (Rochleder, *Ann. Pharm.* 41, 89.) — Bitter almond oil was shaken up with potash and with chloride of iron, then distilled, and the first $\frac{1}{8}$ which passed over, set aside in contact with ammonia. A crystalline substance then separated after a while, and at the end of three weeks, half of the oil was found to be solidified. The solid mass treated with ether, left a residue consisting of white crystalline *azobenzoilide* = $C^{56}N^{3}H^{23}$ [= $C^{84}N^{5}H^{37}$]. (Laurent, *N. Ann Chim. Phys.* 1, 304.)

*Behaviour of crude commercial bitter almond oil containing prussic acid and altered by various influences. with ammonia.* — In contact with aqueous ammonia, the oil slowly becomes thicker, and ultimately quite solid and friable after drying in the air. (Karls, *Pogg.* 10, 609.) When ammoniacal gas is passed through bitter almond oil, the oil becomes pasty, but not solid. (Laurent, *Ann. Chim. Phys.* 62, 24.) — Commercial bitter almond oil covered with an equal volume of strong ammonia was converted in four weeks into a yellow resinous mass consisting of: 1. *Hydrobenzamide,* $C^{42}N^2H^{18}$; — 2. *Benzyhydramide,* $C^{44}N^2H^{18}O^2$; — 3. A body [azobenzoilide?] sparingly soluble in ether, very sparingly in alcohol; — 4. *Azobenzoyl,* $C^{42}N^2H^{15}$; — 5. *Benzoylazotide,* $C^{30}N^2H^{12}$. (Laurent, *Ann. Chim. Phys.* 66, 18; Laurent & Gerhardt, *Compt. Chim.* 1850, 113.)— Bitter almond oil obtained from almond paste by vapour-distillation from above downwards, which had a yellow colour but turned brown after a while, was left in contact with ammonia for four weeks: it then became brown and viscid, did not yield either hydrobenzamide or benzhydramide when treated with boiling ether, but after being treated with ether and boiling alcohol, left a residue of amorphous *azobenzoide,* $C^{84}N^5H^{33}$. (Laurent, *Ann. Chim. Phys.* 69, 790.) — Crude bitter almond oil was distilled by itself, and the first two-thirds of the distillate set aside with ammonia for 14 days, and repeatedly shaken. The whole then solidified into a mass consisting: 1. Of Azobenzoyl; — 2. Needles dissolving with tolerable facility in alcohol; — 3. An oily substance. Another portion of the same oil, spread over the flat bottom of a vessel and covered with ammonia, solidified after eight days; cold ether extracted from the solid mass an oily substance, a body crystallising in needles, and azobenzoyl. The white powder which remained undissolved was decomposed by hot ether into insoluble benzoylazotide and azobenzoidin $C^{84}N^5H^{33}$, which crystallised in six-sided prisms. (Laurent, *N. Ann. Chim. Phys.* 1, 302.)

13. By the action of hydrosulphate of ammonia on bitter almond oil, sulphide of benzylene ($=C^{28}H^{12}S^4$) is produced, together with various products containing sulphur and nitrogen, and differing according to the purity of the oil, and also according to the quantity of the hydrosulphate of ammonia and the nature of the liquid in which it is dissolved. — Bitter almond oil freed from prussic acid by potash and chloride of iron, and dissolved in 8 to 10 times its volume of alcohol, yields sulphide of benzylene on being mixed with hydrosulphate of ammonia. (Laurent, *N. Ann. Chim. Phys.* 1, 292.) — Oil purified in the same manner was distilled; the distillate received in three separate portions; and each portion placed in contact with hydrosulphate of ammonia. The first portion became thick in four weeks, without solidifying, and when treated with ether left a white powder. The second portion, in the course of four weeks, was for the most part, converted into sulphide of benzylene; the third portion still remained liquid after four weeks, but on mixing the oily liquid with an equal volume of hydrosulphate of ammonia, it was partially converted into sulphide of benzylene. From the products of the second and third portions, ether extracted an oily body, which became solid when mixed with alcohol and hydrosulphate of ammonia, and a mixture of hydride of sulphozobenzoyl with a substance which crystallised in needles. (Laurent.) — If the distillation of bitter almond oil purified by potash and chloride of iron be interrupted after $\frac{5}{6}$ has passed over, the residue does not yield any sulphide of benzylene when treated with alcohol and hydrosulphate of ammonia. (Laurent, *N. Ann. Chim. Phys.* 1, 292.) — When a boiling mixture of 8 to 10 volumes of

alcohol and 1 or 2 vol. hydrosulphate of ammonia is mixed with a few drops of crude bitter almond oil, a thick oily precipitate is formed, but no sulphide of benzylene.—A mixture of 1 vol. crude bitter almond oil, 1 vol. hydrosulphate of ammonia and 1 vol. ammonia was left to stand for a year; and, when the nearly solid mass was boiled with ether, hydrosulphate of azobenzoyl $C^{42}NH^{19}S^{4}$, was left undissolved in the form of a white powder. (Laurent, *N. Ann. Chim. Phys.* 1, 300.)—When 1 vol. crude bitter almond oil is dissolved in 8 or 10 volumes of alcohol and 1 vol. hydrosulphate of ammonia gradually added, a separation of sulphide of benzylene almost always occurs after a few minutes. Small quantities of hydrosulphate of ammonia added to a boiling alcoholic solution of bitter almond oil immediately produce a copious precipitate of sulphide of benzylene. If cherry-stone oil be used, the liquid sometimes yields on cooling, long radiated needles of a substance not yet further examined, which dissolves readily in boiling alcohol; the solution when evaporated deposits an oil and crystalline scales. (Laurent, *N. Ann. Chym. Phys.* 1, 292.) — A solution of crude bitter almond oil in 5 vol. ether, mixed with 1 vol. hydrosulphate of ammonia, solidifies in the course of 3 or 4 weeks into a crystalline mass, which when recrystallised from ether, yields pure hydride of sulphobenzoyl (thiobenzaldin) $C^{42}NH^{19}S^{4}$. (Laurent, *Instit.* 1840, 302; *N. Ann. Chim. Phys.* 36, 342.) — Crude four-year old peach-leaf oil shaken up with polysulphide of ammonium (Spir. Beguini), deposited after 8—11 hours a reddish yellow mass of waxy consistence, which, when washed with ether, left a residue having the properties of sulphide of benzylene. — The same oil dissolved in pentasulphide of potassium, and the solution shaken up with aqueous ammonia, yielded after a few hours, a yellowish oil which solidified after 8 days. This oil, when pressed in paper, yielded a crystalline, yellowish body, which dissolved in boiling alcohol, and formed a red liquid with oil of vitriol. (Rochleder, *Ann. Pharm.* 37, 346.) — When the mixture of different substances produced by treating bitter almond oil with sulphide of ammonium is distilled, water, ammonia, sulphuretted hydrogen and several oils pass over first, and then an oily distillate consisting of picryl, stilbene, thionessal and lophine. (Laurent, *Rev. scientif.* 18, 201.)

14. When bitter almond oil is mixed with *ammonia* and *bisulphide of carbon*, two layers are produced, the upper of which gradually turns red and gives off sulphuretted hydrogen when treated with acid, at the same time that a body soluble in potash separates out; in the lower liquid, colourless, generally granular crystals of sulphocyanobenzylene, $C^{16}NH^{5}S^{2}$, are formed, but generally disappear again if left for some time in the liquid. (Quadrat, *Ann. Pharm.* 71, 13.)

15. Potassium does not eliminate hydrogen from bitter almond oil; but the metal gradually disappears, the oil at the same time being converted into a dark mass. (Löwig, *Lehrbuch*, 2, 638.) — 16 and 17. Bitter almond oil heated with *urea* yields a solid mass of benzoylureid:

$$3C^{14}H^{6}O^{2} + 4C^{2}N^{2}H^{4}O^{2} = C^{50}N^{8}H^{26}O^{8} + 6HO,$$

and with aniline, benzoylanilide:

$$C^{14}H^{5}O^{2} + C^{12}NH^{7} = C^{26}NH^{11} + 2HO.$$

(Laurent & Gerhardt, *Compt. Chim.* 1850, 117.)

*Combinations.* *a.* With *water.* Bitter almond oil dissolves in 30 parts of cold water.

*b. With Bisulphite of Ammonia.* — *Sulphite of Benzosum and Ammonium.* — With a saturated solution of bisulphite of ammonia, bitter almond oil mixes in all proportions. The resulting compound cannot however be obtained in the solid state. It appears to be capable of dissolving an excess of bitter almond oil, inasmuch as, on adding water to a solution of a large quantity of bitter almond oil in bisulphite of ammonia, part of the oil separates out. — Ammonia renders the solution turbid, and after a while throws down a body having the properties of hydrobenzamide. (Bertagnini.)

*c. With Bisulphite of Potash.* — When bitter almond oil is shaken up with an aqueous solution of bisulphite of potash of 20—30° Bm., a crystalline magma is almost immediately formed, with spontaneous rise of temperature. The crystalline mass is left to drain on a filter, then dried on a porous tile, washed with cold alcohol, and dissolved as quickly as possible in boiling alcohol; as the liquid cools, the compound separates in crystalline laminæ.

When crystallised from a dilute solution, it forms beautiful crystalline laminæ. It dissolves very easily in pure water, very sparingly in water containing alkaline sulphites, and is nearly insoluble in concentrated solutions of those salts. In cold alcohol it dissolves sparingly, in boiling alcohol readily.

The crystals do not change by exposure to the air. The aqueous or alcoholic solution is decomposed by boiling. Dilute acids do not act upon the compound at ordinary temperatures, but on heating the liquid, bitter almond oil separates. Alkalies decompose the compound, with formation of an alkaline sulphite and separation of bitter almond oil. (Bertagnini.)

*c. With Bisulphite of Soda.* — Bitter almond oil shaken up with 3 or 4 times its volume of a concentrated solution of bisulphite of soda, quickly forms a crystalline magma containing all the bitter almond oil. This crystalline mass is dried and repeatedly crystallised from hot alcohol of 50 per cent. — The compound forms small white aggregated prisms having a faint odour and taste of bitter almond oil and sulphurous acid. Dissolves readily in water, is insoluble in cold alcohol, sparingly soluble in hot alcohol and dissolves pretty readily in hydrated alcohol. (Bertagnini.)

| | | | Bertagnini. |
|---|---|---|---|
| NaO | 31 | 14·14 | 14·15 |
| 14 C | 84 | 38·36 | 38·16 |
| 8 H | 8 | 3·65 | 3·70 |
| 2 S | 32 | 14·61 | 14·72 |
| 8 O | 64 | 29·24 | 29·27 |
| $C^{14}H^{6}O^{2} + NaO,2SO^{2} + 2Aq$ | 219 | 100·00 | 100·00 |

[May be regarded as sulphite of benzosum and sodium $\left.\begin{matrix}C^{14}H^{5}\\Na\end{matrix}\right\}2SO^{2} + 3Aq$. (Gerhardt.)]

The aqueous solution is decomposed by boiling, the oil separating and sulphurous acid gas escaping; the addition of free acids accelerates the

decomposition. Dilute acids do not act upon the compound at ordinary temperatures. Caustic alkalies and their carbonates produce turbidity, and separate the oil. — Iodine and bromine dissolve without colour in the aqueous solution, sulphate of soda being formed and the oil separated.

The compound may be preserved without alteration in closed vessels, and changes but very slowly in contact with the air. When heated in the air, it is decomposed without charring, bitter almond oil volatilising, and the sulphite being oxidised. In a stream of hydrogen, it gives off water and bitter almond oil, even below 100°. Nitric acid converts the sulphite into sulphate and separates the oil.

The aqueous solution forms with chloride of *barium* a copious precipitate soluble in hydrochloric acid, and containing a portion of the oil. *Lead* and *silver*-salts are precipitated in like manner.

*e. With Bichloride of Tin*, bitter almond oil yields a compound which forms fine crystals, but is difficult to purify and decomposes when dried in the air or in vacuo. (Löwig. *Compt. rend.* 21, 371; abstr. *J. pr. Chem.* 37, 480.)

*f. With Hydrocyanic acid.* — When bitter almond water mixed with hydrochloric acid is evaporated at a temperature short of 100°, this compound separates, when only a small quantity of liquid is left, in the form of a yellowish oil, which may be freed from adhering hydrochloric acid by repeated agitation with water, and dried in vacuo over oil of vitriol.

Yellowish oil, nearly inodorous and having a bitter taste. Boils at 170°. Sp. gr.=1·124. Dissolves sparingly in water. (Völckel.)

| | | | Völckel. |
|---|---|---|---|
| 16 C | 96 | 72·18 | 71·98 |
| N | 14 | 10·53 | 11·01 |
| 7 H | 7 | 5·26 | 5·34 |
| 2 O | 16 | 12·03 | 11·67 |
| $C^{14}H^{6}O^{2},C^{2}NH$ | 133 | 100·00 | 100·00 |

It is partially decomposed even at 100°, and when boiled is resolved into hydrochloric acid and bitter almond oil. Potash immediately forms cyanide of potassium and liberates the bitter almond oil. — When the compound is evaporated with hydrochloric acid, water is taken up, and sal-ammoniac and mandelic acid produced. (Völckel.)

It dissolves readily in alcohol and ether. (Völckel.)

*g. With Cyanic acid.* — When cyanic acid vapours are passed into bitter almond oil, great heat is evolved, and a white heavy body separates which increases on addition of ether. — White powder soluble in alcohol and crystallising therefrom. (Liebig, *Ann. Pharm.* 23, 140.)

*h.* Bitter almond oil dissolves in all proportions in *alcohol* and *ether*.

*Appendix to Bitter Almond Oil.*

*Laurel-oil.* — From the fresh leaves of *Prunus Laurocerasus.* Light yellow, heavier than water, having a strong balsamic taste and smell. (Spandaw de Cellié.) — In contact with the air, it is converted into benzoic acid, and likewise yields this compound in contact with moist chlorine gas. (Stange, *Repert.* 14, 329.) — When treated with lime-water and afterwards with chloride of iron, it forms prussian blue. (Roloff, *A. Gehl.* 1, 662.)

*Peach-leaf oil* contains, in addition to bitter almond oil, an oil having the odour of the fresh leaves and fruit of the peach, quite different from that of bitter almond oil. (Winckler, *Repert.* 67, 159.) Produces benzoic acid. (Bragnatelli, *Ann. Chim.* 96, 96.)

*Oil of the Portugal Laurel.* — May be obtained from the bark, leaves, flowers and seeds. — Transparent, colourless oil, heavier than water. Contains hydrocyanic acid and produces benzoic acid. (Giese.) Contains a peculiar volatile oil, which has a pungent disagreeable odour and does not form benzoic acid when exposed to the air. (Winckler, *Repert.* 67, 1, 56.)

*Bitter almond water; Laurel-water; Cherry-water; Aqua amygdalarum amararum; Aqua laurocerasi; Aqua cerasorum* — are essentially aqueous solutions of bitter almond oil containing prussic acid, as they are generally obtained, together with bitter almond oil, in the distillations of parts of plants containing amygdalin and emulsin. (According to Winckler, *Repert.* 52, 289, they contain cyanide of benzoyl.) — For the preparation of these liquids the following directions have been given:

*a Bitter almond water.* — 1. The residue of 2 pounds of bitter almonds completely freed from fixed oil by pressure between hot iron plates, is stirred up to a thin paste with cold water in a distillatory apparatus which admits of being closed, and distilled after 24 hours digestion; the distillation is best performed by means of steam (compare p. 21) or in a chloride of calcium bath. Two pounds of the distillate are collected. (Geiger.) — 2 pounds of bitter almonds freed from fixed oil by cold pressing, are stirred up with 10 lbs. of water, 4 oz. of highly rectified alcohol added, and the mixture distilled till 2 lbs. of liquid have passed over. (*Pharmacopbor.*) The addition of alcohol before the distillation is said by some to diminish the amount of prussic acid in the distillate; others on the contrary maintain that a stronger water is thereby obtained. To these prescriptions, are annexed various appendices, which for the most part directly contradict each other. Compare Gessler (*N. Br. Arch.* 10, 50), Mohr, *Commenta zur pr. Pharmacopoe*, §. 210), Pauls (*N. Br. Arch.* 48, 154.) According to the Parisian pharmacopœia, a double quantity, and according to the Saxon, a treble quantity of water should be distilled off.)

Notwithstanding every precaution, bitter almond water is often obtained of different composition and strength by the same mode of preparation. In general, it is a more or less milky liquid smelling and tasting strongly of bitter almond oil containing prussic acid. The addition of ammonia produces a strong milky turbidity, the more quickly as the liquid is stronger. (Veltmann, *Ann. Pharm.* 34, 235); Lepage, *J. Chim. méd.* 24, 371.) — (According to Weber, it is not altered by ammonia *N. Br. Arch.* 35, 32.) — Its therapeutic action depends on its amount of prussic acid as well as of bitter almond oil. According to Duflos (*Pharm.*

*Centralblatt*, 1837, 560), it contains on the average 1·2 per cent. of bitter almond oil containing prussic acid or 0·173 p. c. of the acid. The Prussian pharmacopœia requires that it shall contain 0·14 per cent. of prussic acid.

*b. Laurel water.* — 2 pts. of the fresh leaves of the common laurel (*Prunus laurocerasus* or *Cerasus laurocerasus*) are distilled with water and 3 pts. of the distillate collected. (Geiger.) — Exhibits the properties of bitter almond water — Mixed with ammonia, it becomes turbid after some time only and in a less degree than bitter almond water. (Veltmann, *Ann. Pharm.* 34, 235; Oswald, *N. Br. Arch.* 38, 160.) Weber found exactly the contrary. — According to Lepage, laurel-water behaves with ammonia in the same manner as bitter almond water (*J. Chim. méd.* 24, 365.) — Leaves gathered in different years and seasons yield various amounts of prussic acid. (Bischoff, *Pharm. Centralbl.* 1841, 889.)

*c. Cherry-water. Aqua cerasorum nigrorum.* — 20 lbs. of wild cherries are bruised, together with their kernels, water poured upon the mass, and 20 or 30 lbs. of the liquid distilled off after 24 hours. — The distillate exhibits the properties of very weak bitter almond water. Winckler (*Repert.* 65, 19) distilled 45 lbs. of ripe black wild cherries, containing about 1·2 lb. of kernels with 80 lbs. of water, till 30 lbs. of liquid had passed over, and the last portions of the distillate were nearly inodorous; the distillate gave 30 grains of bitter almond oil containing prussic acid equivalent to 6·1 p. c. cyanogen.

*Valuation of Bitter almond water, Laurel water, &c.* — Since it is assumed that the efficacy of bitter almond water is proportional to its amount of hydrocyanic acid, the valuation is limited to the estimation of the latter. This is best effected by Liebig's method. (*Ann. Pharm.* 77, 102.) The water to be estimated is mixed with a quantity of caustic potash sufficient to produce a strong alkaline reaction, then diluted with pure water till the turbidity arising from suspended oil-drops disappears, and a dilute solution of nitrate of silver (containing $\frac{1}{2}$ grm. of silver in 100 cub. cent. of the liquid) added from a burette till a permanent precipitate of cyanide of silver is produced. 1 At. silver thus precipitated is equivalent to 2 At. hydrocyanic acid in the liquid. Or 62 grains of fused nitrate of silver are dissolved in 5937 grains of water; a sufficient quantity of this solution — 300 grains of which contain 1 grain of anhydrous prussic acid — counterpoised in a balance; and this solution added by drops to the liquid under examination, previously mixed with caustic potash and a few drops of solution of common salt, till a turbidity is produced which does not disappear on stirring. The amount of prussic acid is then calculated from the loss of weight of the silver-solution. (Compare vii, 397.)

*Decompositions.* In well closed bottles completely filled, bitter almond and laurel water remain unaltered, exhibiting, after the lapse of a year, the same amount of hydrocyanic acid as at first, and having deposited only a slight yellowish sediment. (Paton, *J. Chim. méd.* 16, 203; Lepage, *J. Chim. méd.* 24, 377.) In well closed bottles containing air, and more quickly (in four weeks) in bottles covered only with bibulous paper, bitter almond water loses the whole of its hydrocyanic acid and bitter almond oil. The water then contains ammoniacal salts, probably benzoate and formiate of ammonia. Laurel water keeps

longer. (Lepage.) In the yellowish sediment of concentrated bitter almond water, Veling (*N. Br. Arch.* 43, 297) found benzoate of ammonia. According to Winckler, ether extracts from this sediment a substance smelling strongly of bitter almonds, and leaves another body which agrees in composition with the compound $C^{42}H^{18}Cy^{2}O^{4}$, obtained by Zinin from bitter almond oil and potash. (*Repert.* 92, 328.)

1. Tincture of *iodine* added in sufficient quantity to bitter almond water or laurel water (15—20 drops to 30 grammes of water) forms a limpid mixture which reddens litmus strongly, and does not produce a blue colour with starch. When the mixture is evaporated to one-fourth, oily drops separate, which, if the iodine is not in excess, are colourless, pungent, taste and smell like bitter almond oil, dissolve in ether and alcohol, and yield iodine when treated with nitric acid (they are probably a mixture of iodide and cyanide of benzoyl; the liquid contains hydriodic acid.) (Lepage.) — 2. Two or three drops of *bromine* impart to bitter almond or laurel-water a slight colour and smell; the mixture exhibits reactions similar to that which is formed with iodine. (Lepage.) — 3. A solution of *sulphate of copper* strongly supersaturated with ammonia and added by drops to the water, immediately produces a milky turbidity, which in an hour or two, changes to a copious flocculent precipitate: after the liquid has been shaken, a yellowish resinous matter collects on the surface and in the course of 24 or 48 hours settles to the bottom and may be separated by filtration; it is easily fusible, soluble in alcohol and ether, and does not contain copper (probably a mixture of hydrobenzamide, benzhydramide, azobenzoilide, &c.).— The filtrate is colourless, and, if the copper has not been added in excess, does not coat iron with copper even after the ammonia has been expelled by boiling, although it contains the whole of the copper that has been added. (Lepage.) — 5. When 1 pt. of *iodide of potassium* is dissolved in at least 600 pts. of bitter almond or laurel-water and a solution of *corrosive sublimate* added by drops, a white precipitate soluble in iodide of potassium is immediately produced; with a larger quantity of iodide of potassium, the precipitate is scarlet. (Lepage.) — 6. *Calomel* is blackened by the water, especially if warm, and yields metallic mercury, corrosive sublimate, cyanide of mercury, sal-ammoniac; and on evaporation, mandelic acid. (Winckler, *Repert.* 37, 388; Prend le Loup, *N. J. Pharm.* 6, 47.) According to Prend le Loup, an oily compound of bitter almond oil and sal-ammoniac is formed at the same time. — 7. A solution of *terchloride of gold* is not reduced by bitter almond water or laurel water, as by other distilled waters. If the mixture be immediately boiled down to $\frac{1}{4}$, it becomes decolorised and yields a slight yellow deposit. The strongly acid liquid is not altered by protochloride of tin (cyanide of gold and hydrochloric acid appear to have been formed.) (Lepage.)

*Distinction between Bitter almond water and Laurel water.* — 30 drops of a solution of chloride of gold, in 100 pts. of water do not exhibit any immediate reaction with either of these waters; but after eight hours the bitter almond water no longer exhibits any yellowish colour, while the laurel water retains its colour for 24 hours. (Lepage.) — The statement of Aschoff, that 0·05 grm. sulphate of quinine mixed with 10 drops of laurel water quickly forms a solid mass, whereas bitter almond water does not exhibit such a reaction, is not confirmed by the observations of Lepage; neither is Riglini's statement confirmed, to the effect that a solution of sulphate of quinine in tartaric acid immediately produces a white turbidity with laurel water, but not with bitter almond water.

## Benzoic Acid. $C^{14}H^{6},O^{4}$.

SCHEELE. *Opusc.* 2, 23; also *Crell. N. Entdeck.* 3, 98.
LICHTENSTEIN. *Crell. N. Entdeck.* 4, 9; also *Crell. Ausz. d. n. Entd.* 1, 319; further 1, 335.
GÖTTLING. *Alm.* 1780, 70.
HERMBSTÄDT. *Crell. Ann.* 1785, 2, 303.
TROMMSDORFF. *Crell. Ann.* 1790, 2, 303.—*A. Tr.* 1, 1, 162.—*N. Tr.* 2, 134.
GIESE. *Scher. J.* 8, 170 and 259.
BUCHOLZ. *N. Gehl* 9, 340.—*Taschenb.* 1810, 50.
HISINGER. *Abhandlungen.* 3, 152; also *Scher. Ann.* 2, 37.
BERZELIUS. *N. Gehl.* 2, 277.—*Ann. Chim.* 94, 315.—*Pogg.* 26, 480; also *Ann. Pharm.* 3, 282.
LECANU & SERRAT. *J. Pharm.* 9, 89; also *N. Tr.* 7, 2, 98.
STOLTZE. *Berl. Jahrb.* 25, 1, 75.
STANGE. *Repert.* 14, 329.
WÖHLER & LIEBIG. *Ann. Pharm.* 3, 249; also *Pogg.* 26, 328.
VOGET. *N. Br. Arch.* 3, 291.
ERDMANN & MARCHAND. *J. pr. Chem.* 13, 422.
F. D'ARCET. *Ann. Chim. Phys.* 66, 99; also *J. pr. Chem.* 13, 477.
MOHR. *Ann. Pharm.* 29, 177.
PLANTAMOUR. *Ann. Pharm.* 30, 349.
EULER & HERBERGER. *Jahrb. pr. Pharm.* 2, 308.
WÖHLER. *Ann. Pharm.* 49, 245.
BARRESWIL & BOUDAULT. *N. J. Pharm.* 5, 265.
DESSAIGNES. *Ann. Chim. Phys.* 17, 50.

***Flowers of benzoin, Benzoeblumen, Benzoesalz, Benzoesäure, Flores Benzoes, Acide benzoique.***

Flowers of benzoin were noticed as early as 1663 by Blaise de Vigenère; Scheele and others pointed out more advantageous modes of preparing them; Wöhler and Liebig determined their true composition.

*Sources.* In gum benzoin, dragon's blood, storax, Peru balsam (*Crell. Chem. J.* 1, 58; Herberger, *Repert.* 65, 219); in Tolu balsam (E. Kopp. *Compt. rend.* 24, 714); and *Opobalsamum siccum*, in resin of Botany Bay (Langier, Bollaert); in oil of marjoram (Göttling, *Taschenb.* 1800, 59); in oil of bergamot (C. J. Fischer, *Br. Arch.* 14, 175); in cinnamon-cassia and oil of cinnamon (Dumenil, *Schw.* 21, 224; Henkel, *Repert.* 4, 383; Buchner, *Repert.* 6, 1; 8, 184; Bollaert, *Quart. J. of Sc.* 18, 349; Schweinsberg, *Mag. Pharm.* 26, 386); in the ripe fruit of the clove-tree (Bollaert, *Quart. J. of Sc.* 16, 378; also *Schw.* 42, 122); in the seed of *Euonymus Europæus* (Schweizer, *J. pr. Chem.* 53, 437); in vanille and calmus root, in the root of *Pimpinella saxifraga* (Bley), and of *Inula helenium* (Rötscher, *Arch.* 30, 169); in trefoil, *Holcus adoratus*, *Anthoxanthum odoratum* (Vogel, *Gilb.* 64, 161; *Kastn. Arch.* 5, 413), *Asperula odorata* (Voget, *Repert.* 66, 248); in sternanis, in myrrh (Brandes), and apparently, according to Braconnot, in *Salvia sclarea.*—In *Castoreum moscoviticum* (Laugier, Batka, Brandes (*N. Br. Arch.* 1, 197) and

*Castoreum canadense.* (Riegel, *Jahrb. pr. Pharm.* 6, 34; Wöhler, *Ann. Pharm.* 67, 360). — In the urine (vid. *Hippuric acid.*)

Occurs as a copula in hippuric acid (Dessaignes), and in populin. (Piria.)

*Formation.* 1. From benzylic alcohol when heated with aqueous chromic acid. (Cannizzaro.) — 2. From bitter almond oil heated with solid hydrate of potash or treated with alcoholic potash (Liebig & Wöhler); by absorption of oxygen, or by oxidation with nitric, iodic, or chromic acid; hence also in the oxidation of cinnamic acid (Dumas, Peligot, Siraon), and of protein-compounds. (Proust, *N. Gehl.* 2, 241; Guckelberger, *Ann. Pharm.* 64, 39.) — 3. In the decomposition of bromide or chloride of benzoyl by water. (Wöhler & Liebig.) — 4. By the continued action of dilute nitric acid upon cumol. (Abel, *Phil. Mag. J.* 32, 25.) — 5. By heating cinnamic acid with hydrate of potash. (Chiozza, *Compt. rend.* 36, 701.) — 6. By the dry distillation of kinic acid. (Wöhler, *Ann. Pharm.* 51, 145.)

*Preparation.* 1. *From Gum benzoin.* — *a.* By sublimation. — The best mode of conducting the process is to lay the coarsely pounded resin on the bottom of a round shallow iron pot, 8 inches in diameter, 2 inches high in the side, and having a piece of coarse bibulous paper stretched over its mouth, and closely cemented at the sides; a cone of thick paper is then tied over it and the vessel gently heated on a sand-bath. — The vapours are purified in passing through the bibulous paper and condense on the inner surface of the cone in beautiful crystals having a faint odour of benzoin. — Or the iron vessel is surmounted with an exactly fitting shallow funnel of tin plate, and on its neck, which is tolerably wide and only an inch high, is placed a capacious box of wood or pasteboard. The more slowly the sublimation takes place, the more abundant is the product; the treatment of 1 pound of gum benzoin takes three or four hours. The quantity of acid obtained amounts to 4 per cent. If the fused resin, after being heated, be broken up and again sublimed, a total product is obtained amounting to 12½ per cent. (Mohr.) — Euler & Herberger (*Jahrb. pr. Pharm.* 2, 305) heated gum benzoin in a retort with a receiver till no more vapours were evolved, dissolved the contents of the receiver in hot water and obtained in this manner 13 or 14 per cent. of tolerably pure benzoic acid. — According to Hatchet, benzoic acid is obtained in beautiful crystals by heating the resin with oil of vitriol Veltmann (*Br. Arch.* 7, 190) obtained by sublimation from the resin, 14·4 per cent. of acid, and by the use of oil of vitriol, 16 per cent. — *b.* When 1 pt. of finely powdered gum benzoin is boiled for two hours with 16 pts. of water, the coagulated resin pulverised and again boiled with 8 pts. of water, and this treatment twice more repeated, the quantity of pure acid obtained from the aqueous solution amounts to 6 per cent. (Euler & Herberger.) — *c.* 1 pt. of gum benzoin is dissolved in 4 pts. of alcohol; the filtered solution mixed with 12 pts. of water; the alcohol distilled off; and the remaining liquid, after separation from the resin, evaporated; the benzoic acid then crystallises out. (Bucholz, *N. Gehl.* 9, 340.) The product thus obtained amounts to 13·8 per cent. (Stolze.) — 1 pt. of gum benzoin is dissolved in 3 pts. of alcohol of 75 per cent.; the liquid exactly neutralized with a solution of carbonate of soda in a treble quantity of alcohol and an eight-fold quantity of water; 2 pts.

more of water then added; the alcohol distilled off; the watery liquid decanted from the resin; the resin washed; and the benzoic acid precipitated from the aqueous solution by sulphuric acid. The product is 18 per cent. of benzoic acid. (Stolze.)—*d.* Pulverised gum benzoin is dissolved, with the aid of heat, in an equal volume of alcohol of 90 or 95 per cent., the liquid while still hot gradually mixed with fuming hydrochloric acid till the resin begins to be precipitated, and the mixture distilled as long as the consistence of the residue permits. The cooled residue is again distilled with water as long as drops of benzoic ether pass over; the distillate containing hydrochloric acid, alcohol, and benzoic ether digested with potash-ley, till the whole of the benzoic ether is decomposed; and the benzoic acid precipitated from the liquid by hydrochloric acid. (Wöhler.)—*e.* A mixture of 4 pts. pulverised gum benzoin and 1 pt. crystallised carbonate of soda is stirred up with water to a thin paste, and heated for three hours with constant stirring, and so gently that the resin does not cake together (to between 40° and 60°); the mass is then boiled up with a larger quantity of water; the liquid decanted; and the coagulated mass of resin washed with water. The liquid containing carbonate of soda, benzoate of soda and the compound of the resin with soda is neutralized at the boiling heat with sulphuric acid; the resin precipitated by a slight excess of that acid; the liquid filtered; and the filtrate treated with sulphuric acid to separate the benzoic acid, which then crystallises on cooling. (Bucholz.)—*f.* Four pts. of pulverised gum benzoin are mixed with 2 pts. of hydrate of lime; the mixture digested for some hours with 40 pts. of water; the liquid finally boiled for half an hour, and the solution containing the benzoate of lime filtered from the insoluble compound of lime and resin. The filtrate together with the wash-water, is strongly concentrated by evaporation, decomposed by excess of hydrochloric acid, and the benzoic acid which crystallises out on cooling is washed with a small quantity of cold water and recrystallised from boiling water. (Scheele.) Equal parts of finely pounded gum benzoin and hydrate of lime are mixed as intimately as possible in a mortar; the mixture boiled for some hours with 40 pts. of water, and filtered; and the filtrate evaporated to one-third and mixed with hydrochloric acid. If a smaller quantity of lime is used, the mixture cakes together, and the extraction of the benzoic acid is imperfect. (Geiger, *Handb. d. Ph.* 5 Aufl. 668.) Lg.—8 pts. of pulverised gum benzoin and 2 pts. of hydrate of lime, stirred up to a thin paste with 16 parts of water, are digested for 24 hours, with frequent agitation and renewal of the evaporated water, then mixed with 100 pts. more of water; the liquid boiled, with constant stirring till about 30 pts. of water are evaporated, and filtered hot; the residue boiled with 50 pts. of water, and the liquid filtered and evaporated, together with the first filtrate, till only 32 pts. of liquid remain. To this residual liquid hydrochloric acid is added, with constant stirring, as long as any white turbidity is thereby produced. The benzoic acid which separates on cooling is recrystallised from 20 times its weight of boiling water. The resin thus treated yields from 12·5 to 18·5 per cent. of acid. (Wittstein.) This method is preferable to the process *e*, inasmuch as it yields a purer and more abundant product. (Berzelius, Euler & Herberger, Frickhinger, Wittstein, *Repert.* 57, 399; Bley & Diesel, *N. Arch.* 43, 17.) Benzoic acid is easily extracted from gum benzoin by means of benzol. (De la Rue & Müller, *Chem. Soc. Q. J.* 10, 31.)

2. *From the haulm of Asperula odorata.* — The powder of the dried haulm gathered in the flowering season, is macerated with 4 pts. of cold alcohol of 85° Tralles, and completely exhausted by pressure and repeated drenching. The liquid, which has a dark green colour, with red-brown iridescence, is distilled to $\frac{1}{8}$; and the residue, which has an acid reaction, and an agreeable odour of melilot, is boiled with water, to separate volatile oil and soft resin, and filtered while hot. The filtrate yields by evaporation, crystallised benzoic acid (from 12 to 15 gr. from 16 ounces of the haulm.) (Voget, *N. Br. Arch.* 3, 291.)

3. *From Hippuric acid.* — This acid is boiled for half an hour with strong hydrochloric acid, and the benzoic acid thereby separated is washed with cold water. (Dessaignes.)

The acid prepared by sublimation, according to Mohr's directions, and that which is obtained by the process 1, *d*, is pure, with the exception of traces of a volatile oil, which imparts to it an odour like that of vanille, and is considered of importance in its pharmaceutical applications. The acid obtained by the other methods is sometimes coloured. It may be purified from odorous or colouring matters by the following processes: *a*. By sublimation. This process however does not quite remove the odour. — *b*. By digesting its solution in water (or in alcohol according to Dörfurt) with charcoal. (Stolze, Löwitz.) — *c*. By recrystallisation from dilute sulphuric acid, which retains the oil. (Righini, Winckler, Euler & Herberger.) — *d*. By solution in alcohol and precipitation with water. (Giese.) — *e*. 1 pt. of the crude acid is suspended in 8 pts. of water, and ammonia added till it dissolves; the solution digested with animal charcoal which has been purified by hydrochloric acid; the solution filtered and decomposed by hydrochloric acid; and the acid thereby separated, after being washed with cold water and pressed, is dissolved in alcohol and precipitated therefrom by water. (Janssens, *J. Chim. méd.* 18, 263.) — *f*. When the crude acid is combined with lime, and carbonic acid gas passed through the solution, carbonate of lime is precipitated together with resin; and on evaporating the filtrate to dryness, dissolving the residue in water, and decomposing the solution with hydrochloric acid, pure benzoic acid is obtained. (Bouillon Lagrange, *J. Pharm.* 7, 204.)

*Properties.* 1. From a solution of neutral benzoate of ammonia, benzoic acid crystallises by spontaneous evaporation of the ammonia, in beautiful right rhombic prisms. (Wackenroder, *J. pr. Chem.* 23, 204.) [Was not this the acid salt? L.] Sublimed benzoic acid forms white opaque needles and laminæ, having a pearly lustre; according to Laurent, six-sided prisms, derived from rhombs of 40° and 140°. (*Rev. scient.* 9, 33.) From solution in oil of cinnamon, the acid crystallises in transparent six-sided prisms having two of their lateral faces broader than the rest. (Buchner.) When the acid crystallises by cooling from a hot aqueous solution, it forms needles, but by spontaneous evaporation, it separates in laminæ. Berzelius, *Lehrbuch*, 4, 312.) — Vapour-density 4·27. (Mitscherlich.) — Melts at 120·5°, like fat, and crystallises in radiated masses on cooling; at 154° it begins to evaporate quickly, and at 239° it boils. — Melts at 121·4°; sp. gr. of the liquid acid 1·0838 at 121·4° compared with that of water at 0° as unity. Boiling point 249·2° at 740 mm. (H. Kopp. *Ann. Pharm.* 94, 302.). — The vapours excite tears and coughing. The acid reddens litmus, but not violet juice. In the pure state it is inodorous. Its taste is faint, but persistently sour and warm.

| | | | Berzelius. | Wöhler & Liebig. | Erdmann & Marchand. | Dumas & Stas. | Deville. |
|---|---|---|---|---|---|---|---|
| 14 C | 84 | 68·85 | 68·85 | 69·02 | 68·83 | 68·96 | 69·0 |
| 6 H | 6 | 4·92 | 4·99 | 5·03 | 4·97 | 4·95 | 5·4 |
| 4 O | 32 | 26·23 | 26·16 | 25·95 | 26·20 | 26·09 | 25·6 |
| $C^{14}H^{6}O^{4}$ | 122 | 100·00 | 100·00 | 100·00 | 100·00 | 100·00 | 100·0 |

| | Vol. | Density. |
|---|---|---|
| C-vapour | 14 | 5·8240 |
| H-gas | 6 | 0·3658 |
| O-gas | 2 | 2·2186 |
| Benzoic acid vapour | 2 | 8·4084 |
| | 1 | 4·2042 |

Erdmann & Marchand analysed the acid from horse-urine; Deville, that from Tolu-balsam.

The radical theory assumes a hypothetical anhydrous benzoic acid = $C^{14}H^{5}O^{2}$ = Bz. —According to Mitscherlich, benzoic acid is a conjugated compound of benzol and carbonic acid: $C^{14}H^{6}O^{4} = C^{12}H^{6} + 2CO^{2}$.—Considered as a derivation of the water-type $H^{2}O^{2}$, benzoic acid is a hydrate of benzoyl = $\left.\begin{matrix} C^{14}H^{5}O^{2} \\ H \end{matrix}\right\} O^{2}$.

*Decompositions.* When benzoic acid is heated in a retort with coarsely pounded pumice-stone, and the vapours passed through a red-hot tube filled with fragments of pumice-stone, it is completely resolved by slow decomposition, into carbonic acid gas and benzol. If too strong a heat is applied, there are likewise formed empyreumatic products, naphthalin, carbonic oxide gas and charcoal. (Barreswil & Boudault, *N. J. Pharm.* 5, 265.) — Bouillon Lagrange (*J. Pharm.* 7, 200; *N. Tr.* 6, 2, 343) heated benzoic acid in a retort with ignited alumina; at first needles sublimed; then yellow granules, with evolution of carburetted hydrogen and carbonic acid, and an odour of prussic acid. In one distillation, an oil passed over having the odour of bitter almond oil [benzol ?]. — When benzoic acid vapours are passed through a red-hot tube filled with iron, a yellow empyreumatic oil is produced, which smells of almonds, and when distilled at the heat of the water-bath, yields a residue of tar and a distillate of benzol. At a gentle heat, carbonic acid is also produced; at a stronger heat, carbonic oxide. (F. d'Arcet, *Ann. Chim. Phys.* 66, 97.)

2. Benzoic acid heated in contact with the air, burns away without residue, and with a bright fuliginous flame. — With a spiral of platinum wire, vapour of benzoic acid exhibits slow combustion. (H. Miller, *Ann. Pharm.* 12, 21.)

3. Dry *chlorine* gas acts but very slowly upon dry benzoic acid in the shade; but in sunshine there is gradually formed a moist, tough, gummy, reddish mass, from which carbonate of potash extracts chlorobenzoic acid, leaving a brown red substance, which becomes resinous on exposure to the air, has a peculiar odour distantly resembling that of benzoin, and contains chlorine. (Herzog, *N. Br. Arch.* 22, 15.) — In presence of water, benzoic acid is not perceptibly decomposed by chlorine. (Liebig.) — When chlorine gas is passed into a hot aqueous solution of benzoic acid, various acids are produced, in which 1, 2 or 3 At. hydrogen are replaced by chlorine. (Stenhouse, *Ann. Pharm* 55, 10.) — When a solution of benzoic acid in excess of potash is saturated with chlorine gas, chloroniceic acid $C^{12}ClH^{5}O^{4}$ (xi, 176) is produced. (St.

Evre, *N. Ann. Chim. Phys.* 25, 486.) — 4. Liquid *bromine* placed together with benzoic acid in a closed vessel and exposed to the sun's rays, acts more quickly than chlorine gas, producing a friable yellow mass, from which carbonate of potash extracts *bromobenzoic acid*, and separates a greenish oil containing bromine, which becomes solid and resinous on exposure to the air. (Herzog.)

5. Benzoic acid shaken up with cold strong *nitric acid* dissolves but sparingly; it rises to the surface of the liquid and does not form any deposit (of nitrobenzoic acid). (E. Kopp, *Ann. Chim. Phys.* 1849, 149.) — When benzoic acid is heated with nitric acid, *nitrobenzoic acid* and water are formed:

$$C^{14}H^5O^4 + NO^5 = C^{14}(NO^4)H^5O^4 + HO.$$

(Mulder, *J. pr. Chem.* 19, 362.) The action takes place immediately: if nitrous vapours are at the same time given off, they arise from the action of the nitric acid on the nitrobenzoic acid. (Mitscherlich, *J. pr. Chem.* 22, 196.) — When benzoic acid is distilled with nitric acid, a small quantity of nitrous gas is given off before the liquid begins to boil; but this evolution of gas soon ceases, and the benzoic acid dissolves with yellow colour; towards the end of the action nitrous gas is again given off in large quantity. The distillate consists for the most part of nitric acid having an odour of prussic acid, which however cannot be detected in it by reagents; the residue contains benzoic acid [nitrobenzoic acid; L.] and traces of oxalic acid. (Bouillon Lagrange, *J. Pharm.* 7, 200.)

6. Benzoic acid boiled with aqueous *chloride of lime* yields three different acids in which 1, 2 or 3 At. hydrogen are replaced by chlorine; $C^{14}ClH^5O^4$, $C^{14}Cl^2H^4O^4$ and $C^{14}Cl^3H^3O^4$. The same reaction is produced when benzoic acid is boiled with chlorate of potash and hydrochloric acid. (Stenhouse, *Ann. Pharm.* 55, 10.) — Field (*Ann. Pharm.* 65, 55) by boiling benzoic acid with chlorate of potash and hydrochloric acid, obtained chlorobenzoic acid, $C^{14}ClH^5O^4$.

7. *Pentachloride of phosphorus* does not act upon benzoic acid in the cold, but violently at a gentle heat; hydrochloric acid escapes, and a mixture of oxychloride of phosphorus and chloride of benzoyl is produced (Cahours):

$$PCl^5 + C^{14}H^6O^4 = PCl^3O^2 + C^{14}H^5ClO^2.$$

8. With anhydrous *sulphuric acid*, benzoic acid forms sulphobenzoic acid. In oil of vitriol it dissolves without decomposition.

Aqueous chromic acid is not reduced by benzoic acid.

9. *Potassium* and *sodium* decompose benzoic acid at temperatures considerably below their melting points, charcoal being separated and the metals oxidised: the action is not attended with emission of light.

10. In the *animal organism*, benzoic acid is converted into hippuric acid. (Wöhler, Ure, Keller, Garrod, Schwarz, Marchand.)

*Combinations.* Benzoic acid dissolves sparingly in cold water (in 200 pts, according to Bucholz; in 480 pts., according to Lichtenstein; in 500 pts., according to Bergmann); it dissolves in 24 pts. of boiling water. (Bergmann, Lichtenstein, Dirfurt); in 124·5 pts. (Bucholz); in 30 pts. (Trommsdorff.) It dissolves readily in water to which 1½ pts. phosphate or 4 pts. sulphate of soda have been added. (Ure, *Repert.* 75,

64.) Benzoic acid dissolves readily in oil of vitriol, and is precipitated unchanged from the colourless solution by water.

*Benzoates.*—Benzoic acid decomposes carbonates. From an alcoholic solution of benzoate of potash, however, carbonic acid gas throws down carbonate of potash. (Limpricht & List.) — Most acids separate benzoic acids from its salts. — Most of the benzoates are crystallisable. They contain 1 At. base to either 1 or 2 At. acid. Most of the normal (monobasic) benzoates yield by dry distillation, benzol, benzophenine, naphthalin (or compounds polymeric with it), undecomposed benzoic acid, and a metallic carbonate. — When they are heated with phosphoric acid, benzoic acid sublimes undecomposed. — Nearly all benzoates are soluble in water, and most of them dissolve readily. Many are likewise soluble in alcohol. As the benzoates are for the most part more soluble in water than the free acid, the acid is separated from their solutions on the addition of strong acids, a milky turbidity being first produced, and the benzoic acid afterwards crystallising out. — The more sparingly soluble benzoates dissolve readily, according to Lecanu & Serbat (*J. Pharm.* 9, 89) in aqueous acetate of potash or soda, and in nitrate of soda, but not in nitrate of potash, or in sulphate or hydrochlorate of soda.

*Benzoate of Ammonia.* — *a. Normal.* — Benzoic acid is dissolved nearly to saturation, in warm concentrated aqueous ammonia, and the solution left to cool,—or a more dilute solution of benzoic acid in ammonia is left to evaporate and ammonia added to it from time to time. The salt crystallises with difficulty in thread-like crystals; it has a sharp taste. According to Trommsdorff, it may be sublimed; but according to Berzelius, it is converted into the acid salt, even during the evaporation of its solution. When heated in a retort, it is converted into benzonitrile and water:

$$C^{14}(NH^{4})H^{5}O^{4} = C^{14}H^{5}N + 4HO.$$

When heated, it melts, gives off vapours of benzoic acid, and does not leave any residue. (Ure, *Repert.* 75, 64.) — When passed over baryta at a dull red heat, it yields benzonitrile and a crystalline body. (Laurent & Chancel; *Compt. chim.* 1849, 117.) — It deliquesces in the air (Lichtenstein), dissolves readily in water and alcohol (Trommsdorff), but less readily in alcohol than the potash-salts. (Berzelius.)

*b. Acid.* — Produced during the spontaneous evaporation of a solution of the normal salt; it then separates in large irregular crystals, a portion however efflorescing on the edges. When the solution of *a* is boiled, ammonia escapes, and the acid salt separates in needles united in feathery tufts or in granules, accordingly as the solution is more or less quickly cooled. It dissolves sparingly in water and is less soluble in absolute alcohol than the normal salt. (Berzelius.)

*Benzoate of Potash.* — *a. Normal.* — Crystallises from a hot-saturated alcoholic solution, in needles united in tufts; or, if it separates from the solution while still hot, it forms laminæ having a pearly lustre. From the aqueous solution, it crystallises with difficulty in needles united in feathery tufts. The solutions effloresce when abandoned to spontaneous

evaporation. — Potash exactly saturated with benzoic acid yields a salt which separates in delicate pointed crystals, and deliquesces in moist air [because it contains free potash: L.]; if a somewhat larger quantity of acid be added, the same crystals are obtained, but they remain dry when exposed to the aid. (Trommsdorff, *A. Tr.* 1, 162.) — Benzoate of potash is difficult to crystallise from water, but crystallises from absolute alcohol in unctuous masses. (Lichtenstein, Berzelius, *N. Gehl.* 2, 277.) — The salt has a sharp, somewhat burning taste. (Berzelius.) — At the heat of the water-bath, it gives off 1 At. water. (Berzelius.) — Dissolves very easily in water. — Distilled with arsenious acid, it yields benzol. (F. d'Arcet.)

*b. Acid.* — Produced in presence of excess of acid. (Berzelius.) It is contained in the residue of the preparation of anhydrous acetic acid from chloride of benzoyl and acetate of potash, and after washing with water, crystallises from solution in boiling alcohol, in beautiful laminæ having a pearly lustre. (Gregory.) — Contains 13·4 p. c. potassium, the formula requiring 13·8 p. c. (Gregory.) — Leaves the normal salt when heated. (Berzelius.)—Dissolves in 10 pts. of water (Berzelius), and in a large quantity of boiling alcohol. (Gregory.)

*Benzoate of Soda.* — Somewhat efflorescent pointed crystals, soluble in water and sparingly soluble in boiling alcohol. (Lichtenstein, Trommsdorff, Berzelius.) — The anhydrous salt treated with protochloride of sulphur yields chloride of benzoyl, together with chloride of sodium, sulphate of soda, and sulphur:

$$2C^{14}H^5NaO^4 + 3SCl = 2C^{14}H^5O^2Cl + NaCl + NaO,SO^3 + 2S:$$

and the chloride of benzoyl, if heated to 150° with excess of the benzoate of soda, forms anhydrous benzoic acid. (Heintz, *Pogg.* 98, 458.)

*Benzoate of Lithia.*—White, opaque, amorphous mass, which dissolves readily in water and does not deliquesce on exposure to the air. (C. G. Gmelin.) — It is easily soluble and dries up to white saline mass which becomes moist when exposed to the air. (Berzelius.)

*Benzoate of Baryta.*—Slender needles, permanent in the air, sparingly soluble in cold, readily in hot water. (Trommsdorff.) — Large tables which become opaque at 100°, and contain 47·07 per cent. of baryta. (Plantamour.) — Gives off 2 At. water at 110°. (Limpricht, private communication.)

| | | | | | Limpricht. |
|---|---|---|---|---|---|
| BaO | 76·6 | .... | 36·90 | ..... | 36·60 |
| $C^{14}H^5O^3$ | 113·0 | .... | 54·43 | ..... | 54·43 |
| 2 HO | 18·0 | .... | 8·67 | ..... | 8·97 |
| $C^{14}BaH^5O^4 + 2Aq$ | 207·6 | .... | 100·00 | ..... | 100·00 |

*Benzoate of Strontia.* — Resembles the baryta-salt. The crystals, when exposed to the air, lose their lustre but do not effloresce: they dissolve sparingly in cold, readily in hot water. (Berzelius.)

*Benzoate of Lime.* — Sometimes forms needles having a silky lustre, and united in bundles or feathery tufts, sometimes granules. (Berzelius.) Long thick needles, having a strong lustre. (Plantamour.)

| | | | Plantamour. |
|---|---|---|---|
| CaO | 28·1 | 17·66 | 17·68 |
| 14 C | 84·0 | 52·80 | 51·85 |
| 7 H | 7·0 | 4·40 | 4·05 |
| 5 O | 40·0 | 25·14 | 26·42 |
| $C^{14}H^{5}CaO^{4}$ + 2 Aq | 159·1 | 100·00 | 100·00 |

Has a sharp and sweetish taste. Becomes liquid when heated, and yields by dry distillation, benzol, benzone (benzophenone according to Chancel), naphthalin, benzoate of lime, and carbonate of lime. (Peligot.) — Dissolves in 29 pts. of cold water. (Bucholz, Lichtenstein.)

*Benzoate of Magnesia.* — Short feathery crystals having a somewhat bitter pungent taste, slightly efflorescent, easily soluble in water. (Lichtenstein, Trommsdorff.)

*Cerous Benzoate.* — Benzoate of potash or ammonia added in excess to the solution of a cerous salt forms a permanent curdy precipitate. (Berzelius,) When hydrated cerous oxide is boiled with an aqueous solution of impure benzoic acid, a compound of cerous oxide, benzoic acid and resin remains undissolved, and the solution when evaporated, first yields crystals of benzoic acid, and then pure cerous benzoate in white crystalline granules. (Berzelius & Hisinger.)

*Benzoate of Yttria.* — Benzoate of ammonia forms with hydrochlorate of yttria a thick precipitate sparingly soluble in water (Hisinger); according to Berzelius, it is insoluble. — Concentrated solutions of yttria-salts do not form an immediate precipitate with alkaline benzoates, but when the mixture is left for some time in a warm place, benzoate of yttria separates in the form of a white powder. Dilute solutions yield the salt after evaporation in small crystalline granules, which, when examined by the microscope, appear to consist of four-sided prisms united in spherical groups. The salt does not appear to contain water. It dissolves in 89 pts. of cold water, more readily in warm water. (Berlin.)

*Benzoate of Glucina.* — *a. Bibasic.* — Precipitated by double decomposition of bibasic glucina-salts with alkaline benzoates; the precipitation is not immediate, but, after a few seconds, a gelatinous precipitate separates, which is not dissolved on addition of water or on boiling.

*b. Monobasic.* — Neutral glucina-salts are not precipitated by alkaline benzoates; but the mixture abandoned to spontaneous evaporation first yields crystals resembling benzoic acid and containing but little glucina, and the mass afterwards solidifies into a jelly which appears to consist of normal benzoate of glucina.

*Benzoate of Alumina.* — Obtained as a curdy crystalline precipitate on mixing a somewhat concentrated solution of an alumina-salt with benzoate of potash. Has a rough taste. Reddens litmus. (Lichtenstein, Trommsdorff.) It dissolves pretty readily in water. (Hisinger.) The hot saturated solution solidifies in a crystalline mass on cooling. (Berzelius.)

*Benzoate of Zirconia.* — Benzoate of potash added to zirconia salts throws down a bluish grey powder, sparingly soluble in water. (Hisinger.)

Alkaline benzoates do not precipitate vanadic salts. (Berzelius.)

*Chromous Benzoate.* — Protochloride of chromium forms with benzoate of potash a light greyish precipitate, which becomes bluish green on exposure to the air. — In vacuo over oil of vitriol, or in a stream of hydrogen at 100°, it gives off water and assumes an ash-grey colour. (Moberg, *J. pr. Chem.* 44, 330.)

| | *Dried.* | | Moberg. |
|---|---|---|---|
| CrO | 36 | 24·16 | 23·47 |
| 14 C | 84 | 56·37 | 56·03 |
| 5 H | 5 | 3·36 | 3·42 |
| 3 O | 24 | 16·11 | 17·08 |
| $C^{14}CrH^5O^4$ | 149 | 100·00 | 100·00 |

*Uranic Benzoate.* — Obtained by double decomposition. Pale yellow, very slightly soluble in water. (Richter.)

*Manganous Benzoate.* — Transparent, colourless needles, which are permanent in the air, taste at first sweet and rough, afterwards bitter, dissolve in 20 pts. of cold water, and are much more soluble in hot water. (John.) Sparingly soluble in alcohol. (Trommsdorff.)

| | | | John. |
|---|---|---|---|
| MnO | 35·6 | 22·59 | 2·4 |
| $C^{14}H^5O^3$ | 113·0 | 71·70 | |
| HO | 9·0 | 5·71 | |
| $C^{14}MnH^5O^4$ + Aq | 157·6 | 100·00 | |

*Arsenious acid* dissolves readily in hot aqueous benzoic acid; the solution yields efflorescent feathery crystals, which have a sour and rather pungent taste, sublime at a moderate heat, are decomposed at a stronger heat, and dissolve readily in hot water. — *Teroxide of antimony* obtained by calcination dissolves readily in aqueous benzoic acid, and yields a white laminar mass permanent in the air, and easily soluble in water and alcohol. (Trommsdorff.) — With *Telluric salts*, benzoate of ammonia forms a white nearly insoluble precipitate. (Hisinger.)

*Benzoate of Bismuth.* — Benzoate of ammonia forms with nitrate of bismuth a white precipitate partially soluble in water. (Hisinger.) — It dissolves when heated with excess of benzoic acid and with water, and separates on cooling in needles which dissolve in water and alcohol, with separation of oxide of bismuth [basic salt?]. (Trommsdorff.)

*Benzoate of Zinc.* — Dendritic, efflorescent crystals which have a rough sweetish taste, and dissolve readily in water and alcohol. (Trommsdorff.) Benzoate of ammonia does not precipitate sulphate of zinc. (Hisinger.)

*Benzoate of Cadmium.* — Aqueous benzoic acid dissolves a very small quantity of hydrated oxide of cadmium; and the solution when evaporated, yields crystals of benzoic acid together with a yellowish powder.

*Stannous and Stannic Benzoates.*—Obtained by double decomposition. White precipitates soluble in water especially if hot, insoluble in alcohol. (Trommsdorff, Hisinger, Berzelius.)

*Benzoate of Lead.*—*a. Tribasic.*—Produced by precipitating basic acetate of lead with benzoate of ammonia, or by treating *b* with ammonia. White powder; anhydrous. (Berzelius.)

| | | | | Berzelius. |
|---|---|---|---|---|
| 3 PbO | 336 | .... | 74·83 | ..... 74 |
| $C^{14}H^{5}O^{3}$ | 113 | .... | 25·17 | ..... 26 |
| $2PbO,C^{14}PbH^{5}O^{4}$ | 449 | .... | 100·00 | ..... 100 |

*b. Monobasic* or *Normal.*—Protoxide of lead dissolves in aqueous benzoic acid; and the solution yields white, shining, crystalline laminæ, soluble in water and alcohol. (Trommsdorff.) By precipitating neutral lead-salts with normal benzoate of potash, a light crystalline powder is obtained which at a temperature somewhat above 100°, melts and gives off 3·79 per cent. (1 At.) of water. It dissolves when boiled with dilute acetic acid, and separates on cooling in shining crystalline scales resembling the free acid. (Berzelius.)

| | | | | Berzelius. |
|---|---|---|---|---|
| PbO | 112 | .... | 47·86 | ..... 46·49 |
| $C^{14}H^{5}O^{3}$ | 113 | .... | 48·28 | ..... 49·66 |
| HO | 9 | .... | 3·86 | ..... 3·85 |
| $C^{14}PbH^{5}O^{4}$ + Aq | 234 | .... | 100·00 | ..... 100·00 |

*Aceto-benzoate of Lead.*—When benzoate of lead is digested with basic acetate of lead, the loose pulverulent precipitate gradually becomes heavy and crystalline, and acetic acid may be detected in it. (Varrentrapp, *Ann. Pharm.* 35, 79.)

| | | | | Varrentrapp. |
|---|---|---|---|---|
| 8 Pb | 894·4 | .... | 80·61 | ..... 81·01 |
| 22 C | 132·0 | .... | 11·94 | ..... 12·09 |
| 11 H | 11·0 | .... | 0·97 | ..... 1·01 |
| 9 O | 72·0 | .... | 6·48 | ..... 5·89 |
| $2PbO,C^{14}H^{5}O^{3} + 2(3PbO,C^{4}H^{3}O^{3})$ | 1109·4 | .... | 100·00 | ..... 100·00 |

*Ferrous Benzoate* crystallises in needles, which effloresce and turn yellow when exposed to the air. They dissolve in water and alcohol. Benzoate of ammonia does not precipitate ferrous salts. (Berzelius.)

*Ferric Benzoate.*—*a. Hyperbasic.*—*a.* If a solution of sesquichloride of iron be mixed with so much ammonia that its colour becomes deep red, and after a few hours a small quantity of sesquioxide remains undissolved at the bottom, and if a neutral benzoate of an alkali be then added, a very bulky flesh-coloured precipitate is formed insoluble in water. It is not decomposed by cold water. (Berzelius.)

| | | | Hisinger. | Thomson. |
|---|---|---|---|---|
| $2\ Fe^2O^3$ | 160 | 25·24 | 24 | 25 |
| $3\ C^{14}H^5O^3$ | 339 | 53·47 | | |
| $15\ HO$ | 135 | 21·29 | | |
| $2Fe^2O^3,3C^{14}H^5O^3 + 15Aq$ | 634 | 100·00 | | |

[Berzelius supposes the salt to contain only 12 At. water, but according to that supposition it should contain 26·34 p. c. ferric oxide. L.]

*β*. Remains undissolved when *b* is treated with cold water. (Berzelius.)

*b*. *Basic*. — When a solution of ferric oxide is mixed with a quantity of alkali sufficient to turn it yellow, and a normal alkaline benzoate then added, a reddish white mass is thrown down, which is insoluble in the saline liquid; when washed on a filter with water, it becomes darker, and a liquid containing an acid salt runs through, while a more basic compound remains on the filter. (Berzelius.)

*c*. *Ter-acid* or *Normal*. — A solution of ferric oxide in aqueous benzoic acid yields yellow crystalline needles which are dissolved by water or alcohol, a basic salt being left behind. (Trommsdorff, Berzelius.)

*d*. *Acid*. — Produced on mixing *b* with water, while *a*, *β* remains undissolved. (Berzelius.)

*Benzoate of Cobalt* and *Benzoate of Nickel* are soluble in water and may be obtained in the crystalline state. The cobalt-salt is red, the nickel-salt green, and both dissolve in alcohol. When the solution of either of these salts is mixed with the oxide or carbonate of the same metal, basic salts are formed. (Berzelius.)

*Cupric Benzoate*. — On mixing an alkaline benzoate with a cupric salt, a bluish precipitate is formed, which acquires a fine green colour when dry, and is somewhat soluble in water. (Berzelius.) Insoluble in alcohol. (Trommsdorff.) When precipitated from a hot solution of sulphate of copper, it forms a loose aggregate of bluish green needles. (Ettling.) It does not contain water. (Mitscherlich.) It dissolves in dilute acetic acid when heated, and crystallises therefrom in small needles. By dry distillation it yields benzol, carbolic acid, benzoic acid, benzoate of phenyl, and an oil which boils at 260° and when heated with oil of vitriol, is resolved into carbolic acid and a crystallisable hydrocarbon, $C^{10}H^4$. (Ettling, List & Limpricht.) At a low temperature, cuprous salicylite remains in the residue. (Ettling.)

*Mercurous Benzoate*. — Formed by precipitating mercurous salts with aqueous benzoic acid or alkaline benzoates. White, very bulky, crystalline precipitate, consisting of slender needles. (Hisinger, Harff.) Acquires a light yellow colour by exposure to light. When heated, it acquires a dark yellow colour, swells up strongly, then turns grey, and ultimately becomes white again. — When it is quickly heated, a sudden glowing of the mass takes place, and a porous charcoal remains behind. At the beginning of the decomposition, benzoic acid sublimes unaltered, so that a basic salt remains behind; afterwards empyreumatic vapours and mercurial vapours are given off. (Burckhardt, *N. Br. Arch.* 11, 250.) The salt sublimes partly undecomposed in white feathery crystals [unless these consist of benzoic acid. Gm.] and moreover yields mercury-vapours and charcoal. (Harff.)

| | | | | Harff. |
|---|---|---|---|---|
| $Hg^2O$ | 208 | 64·75 | | 64·01 |
| $C^{14}H^5O^3$ | 113 | 35·25 | | |
| $C^{14}Hg^2H^5O^4$ | 321 | 100·00 | | |

Insoluble in cold water, in alcohol and in ether. Dissolves in aqueous benzoic acid (Harff); is insoluble in aqueous benzoic acid and in benzoate of ammonia or potash. (Burckhardt.) Dissolves in concentrated solutions of alkaline acetates and common salt. Is decomposed by boiling water (Harff), and alcohol (Burckhardt), with separation of metallic mercury.

*Mercuric Benzoate.* — *a. Basic.* — *α.* When benzoic acid is boiled with water and excess of mercuric oxide, a light white crystalline powder is formed, which is easily separated from the mercuric oxide by levigation. It is insoluble in water and alcohol. According to Trommsdorff, it sublimes in feathery crystals. — *β.* The neutral salt continuously boiled with a concentrated solution of carbonate of potash, carbonate of soda, or phosphate of soda, is converted into a yellow basic salt. Insoluble in water. Aqueous benzoic acid converts it into *b.* (Burckhardt.)

*b. Normal.* — Obtained by precipitating a solution of corrosive sublimate by an alkaline benzoate, or mercuric acetate by aqueous benzoic acid. (Burckhardt.) When mercuric acetate is decomposed by alkaline benzoates, part of the mercuric benzoate remains dissolved in the alkaline acetate. White bulky precipitate gradually becoming crystalline (Harff), made up of slender needles. (Burckhardt.) Does not blacken when exposed to light. (Burckhardt, *N. Arch.* 11, 277.)

| | | | Harff. | Burckhardt. |
|---|---|---|---|---|
| HgO | 108 | 46·95 | 45·33 | 46·00 |
| $C^{14}H^5O^3$ | 113 | 49·14 | | |
| HO | 9 | 3 91 | 3·3 | |
| $C^{14}HgH^5O^4$ | 230 | 100·00 | | |

Sublimes in a glass tube partly undecomposed in feathery crystals [benzoic acid? Gm.], yielding at the same time mercury and charcoal. (Harff.) Resolved by heat into benzoic acid, carbonic acid, carbonic oxide, mercury, and charcoal. (Burckhardt.)

The salt is insoluble in cold water, but dissolves pretty freely in hot water, and separates out unaltered on cooling (Burckhardt); boiling water converts it into an insoluble basic salt which does not dissolve. (Harff.) — Alcohol dissolves a portion of the salt, and separates a basic salt which is converted into oxide by continued boiling. It is insoluble in ether. (Burckhardt.) It dissolves in 370 pts. of alcohol, and is resolved by ether into a basic and an acid salt, which dissolves in 2 pts. of ether. (Harff.)

*Ammonio-mercurous Benzoate.* — Obtained by treating mercurous benzoate with ammonia; the resulting black powder, after being washed and dried contains 80·90 per cent. of mercurous oxide. (Harff.) [The composition of the salt agrees therefore with the formula $3Hg^2O,C^{14}H^5O^3 + NH^3$, which requires 80·21 p. c. mercurous oxide. Harff (*N. Br. Arch* 5, 285) adopts the formula $Hg^2O,C^{14}H^5O^3 + NH^3$, which requires 57·46 p. c. mercurous oxide. L.] The salt

when heated gives off oxygen gas [? Gm.], ammonia, benzoic acid and mercury. Heated with potash, it gives off ammonia. Insoluble in water or alcohol, but dissolves in acetic acid, globules of metallic mercury separating at the same time. (Harff.)

*Ammonio-mercuric Benzoate.* — By treating mercuric oxide with ammonia, a white powder is produced which, after washing and drying, contains 69·92 per cent. of mercuric oxide. (Harff, *N. Br. Arch.* 5, 287.) [The formula $3HgO,C^{14}H^5O^3 + NH^3$ requires 67·78 p. c. of mercury. Harff adopts the formula $Hg^{\prime\prime}O,C^{14}H^5O^3 + NH^3$, which requires 41·22 p. c. of mercurous oxide.] When the salt is heated, mercuric benzoate sublimes [? Gm.], and oxygen gas [? Gm.] escapes together with ammonia. Potash turns it yellow and eliminates ammonia. It is insoluble in water. Dissolves in 1500 pts. of alcohol and 2000 pts. of ether. (Harff.)

*Benzoate of Silver.* — By mixing the solutions of nitrate of silver and an alkaline benzoate, this salt is obtained in the form of a white spongy precipitate; it is also produced by treating oxide of silver with aqueous benzoic acid. (Trommsdorff.) The thick white precipitate becomes somewhat crystalline when heated with water, dissolves completely in a larger quantity of boiling water, and then crystallises in long shining crystalline laminæ, which do not lose their lustre or diminish in weight by drying in vacuo. When heated it melts and swells up, and after the charcoal has burnt away, leaves white crystalline silver. (Wöhler & Liebig.) [The shining silver which remains when benzoate of silver is ignited contains rather a large quantity of carbon. (Liebig & Redtenbacher, *Ann. Pharm.* 38, 130: E. Kopp, *Compt. Chim.* 1849, 158.)]

| | | | Wöhler & Liebig. | Berzelius. |
|---|---|---|---|---|
| Ag | 108 | 47·16 | 47·04 | 46·83 |
| 14 C | 84 | 36·68 | | |
| 5 H | 5 | 2·18 | | |
| 4 O | 32 | 13·98 | | |
| $C^{14}HgH^5O^4$ | 229 | 100·00 | | |

Dissolves in 1·96 pts. of absolute alcohol at 20°. (Mitscherlich, *J. pr. Chem.* 22, 194.)

*Benzoate of Gold.* — Obtained by dissolving teroxide of gold precipitated by potash in hot aqueous benzoic acid. Forms small irregular crystals, permanent in the air, sparingly soluble in water, insoluble in alcohol. (Trommsdorff.) — Hydrochlorate of auric oxide is not precipitated by benzoate of potash. (Berzelius.)

*Benzoate of Platinum.* — Obtained by dissolving platinic oxide in the acid. Yellow, velvety crystals which leave a yellow powder when ignited [? Gm.]; they dissolve sparingly in water and are insoluble in alcohol. (Trommsdorff.) — Benzoate of ammonia does not precipitate platinum-salts. (Hisinger.)

The compounds of benzoic acid with auric and platinic oxides obtained by Trommsdorff, are probably double salts. (Berzelius, *Lehrbuch*, 4, 319.)

In *palladous salts*, benzoate of ammonia produces a white precipitate, soluble in water. (Hisinger.)

Benzoic acid dissolves in 2 pts. of cold and 1 pt. of boiling absolute *alcohol;* in 2.5 pts. of *ether*, whether cold or hot. (Buchholz.) It dissolves readily in *oils* both *fixed* and *volatile*.

*Appendix to Benzoic Acid.*

## 1. Amorphous Benzoic Acid.

E. Kopp. *Compt. chim.* 1849, 154.

*Parabenzoic acid.*

*Formation and Preparation.* When 1 pt. of gum benzoin or Tolu resin is heated with 6 or 8 pts. of nitric acid, not strong enough to form nitrobenzoic acid, a violent evolution of nitric oxide and carbonic acid soon takes place, and the resin swells up to an orange-yellow mass. As soon as the action is finished, the mass is introduced into a capacious retort and distilled, the liquid which passes over being poured back from time to time. The viscid liquid ultimately left in the retort is mixed with 3 or 4 pts. of boiling water, which separates a yellow resin; and the liquid decanted therefrom deposits on cooling, a yellow powder, while picric and nitric acids remain dissolved. The yellow powder is purified from adhering colouring matter by repeatedly dissolving it in hot water and leaving the solution to cool; or it is mixed with milk of lime, whereupon the resinous colouring matter remains undissolved, together with the lime, and the filtrate is precipitated by hydrochloric acid.

*Properties.* When perfectly purified, it forms a white amorphous powder; but it is commonly mixed with a small quantity of a yellow resin which passes with it into all its compounds. It then forms light-yellow crusts and warty crystalline granules (*c*); has a slightly sour aromatic and slightly bitter taste; melts at 113° to a yellowish brown liquid; boils at 256°; becomes covered when exposed to the sun or gently heated, with white crystals of benzoic acid; and when distilled, yields pure crystallised benzoic acid, with a small residue of charcoal. The white powder (*e*) obtained by repeated purification, is converted by distillation into crystallised benzoic acid, without leaving any residue

| | | *a.* | *b.* | *c.* | *d.* | *e.* |
|---|---|---|---|---|---|---|
| 14 C..... | 68·85 | 72·95 | 70·50 | 69·75 | 69·10 | 69·00 |
| 6 H..... | 4·92 | 5·10 | 4·80 | 4·85 | 4·99 | 5·00 |
| 4 O..... | 26·23 | | | | | |
| | 100·00 | | | | | |

When distilled with lime, it yields benzol.

*Combinations.* The acid of composition *c*, forms with bases, salts which are less soluble than those of pure benzoic acid.

The *ammonia-salt* is yellow. The *lime-salt* crystallises in yellow nodules by spontaneous evaporation. The *lead-salt*, obtained by precipi-

tating the lime-salt with neutral acetate of lead, or the soda-salt with nitrate of lead is a yellow, non-crystalline, insoluble precipitate consisting of $2PbO, C^{14}H^{8}O^{3}$ + resin. The *copper-salt* obtained by precipitating the lime-salt with acetate of copper, is of a beautiful green colour, amorphous, and yields by dry distillation, benzoic acid and benzol, leaving metallic copper and charcoal. The *silver-salt* obtained from nitrate of silver and the ammonia-salt, is dark brown and is resolved by boiling with water into an insoluble brown amorphous body, and a soluble portion which crystallizes in dendrites.

The acid dissolves readily in *alcohol* and *ether*.

The compound ether obtained by treating this acid with alcohol and hydrochloric acid is a reddish oil, heavier than water, having an aromatic odour and bitter taste; when distilled after drying, it yields pure benzoate of ethyl.

## 2. Carbobenzoic Acid. $C^{15}H^{6}O^{4}$.

PLANTAMOUR. *Ann. Pharm.* 30, 341.

[Benzoic acid, with a small quantity of cinnamic acid? Gm.]

*Preparation.* Cinnamein is mixed with concentrated alcoholic potash; the soapy mass diluted with water, and repeatedly distilled with fresh portions of water till all the cinnamic ether and peruvin have passed over; the residue dissolved in water; the solution decomposed by hydrochloric acid; and the cinnamic and carbobenzoic acids thus separated are washed with cold water and dissolved in hot water, whence the cinnamic acid crystallises on cooling. The mother-liquor yields after evaporation, first a mixture of laminar cinnamic acid and cauliflower-like carbobenzoic acid; the last mother-liquor yields only carbobenzoic acid.—2. From the mixture of cinnamic and carbobenzoic acids precipitated by hydrochloric acid, pure carbobenzoic acid sublimes between 120° and 150°.

*Properties.* Crystalline grains grouped in masses like cauliflower-heads. Melts at 150°; boils at 250°; sublimes a little below its melting point in granules united in cauliflower-heads and destitute of lustre.

| | | | Plantamour. |
|---|---|---|---|
| 15 C | 90 | 70·71 | 70·37 |
| 6 H | 6 | 4·62 | 5·18 |
| 4 O | 32 | 24·67 | 24·45 |
| $C^{15}H^{6}O^{4}$ | 128 | 100·00 | 100·00 |

*Combinations.* More soluble in water than benzoic acid.

The carbobenzoates crystallise in cauliflower-like masses, which cake together when heated.

*Carbobenzoate of Baryta.*—Obtained by dissolving the crystallised acid in hot baryta-water. Anhydrous.

| | | | Plantamour. |
|---|---|---|---|
| BaO | 76·6 | 38·41 | 40·07 |
| 15 C | 90·0 | 46·49 | 46·20 |
| 5 H | 5·0 | 2·53 | 2·96 |
| 3 O | 24·0 | 12·57 | 10·77 |
| $C^{15}BaH^{5}O^{4}$ | 195·6 | 100·00 | 100·00 |

*Carbobenzoate of Lime.* — Prepared like the baryta-salt.

| | | | Plantamour. |
|---|---|---|---|
| CaO | 28·1 | 18·00 | 18·87 |
| 15 C | 90·0 | 57·98 | 57·96 |
| 5 H | 5·0 | 3·79 | 3·81 |
| 3 O | 24·0 | 20·23 | 19·36 |
| $C^{15}CaH^{5}O^{4}$ | 147·1 | 100·00 | 100·00 |

*Carbobenzoate of Lead.* — Becomes waxy at 100°.

| | | | Plantamour. |
|---|---|---|---|
| PbO | 112 | 48·03 | 48·29 |
| 15 C | 90 | 39·48 | 39·31 |
| 5 H | 5 | 2·14 | 2·29 |
| 3 O | 24 | 10·35 | 10·11 |
| $C^{15}PbH^{5}O^{4}$ | 231 | 100·00 | 100·00 |

*Carbobenzoate of Silver.* — By precipitating the ammonia-salt with nitrate of silver. Flocculent precipitate. Decomposed by evaporation.

| | | Plantamour. |
|---|---|---|
| Ag | 45·34 | 45·42 |
| 15 C | 38·46 | 37·89 |
| 5 H | 2·09 | 2·52 |
| 4 O | 14·11 | 14·17 |
| $C^{15}AgH^{5}O^{4}$ | 100·00 | 100·00 |

Carbobenzoic acid dissolves readily in *alcohol* and *ether*.

## 3. Hypobenzoylous Acid.

LOWIG & WEIDMANN. *Pogg.* 50, 105.

*Formation and Preparation.* The mixture obtained by heating benzoate of ethyl with sodium (p. 61), is washed with anhydrous ether, which leaves undissolved a saline mass consisting of ethylate and benzoate of sodium. The dark brown liquid having been freed from ether by distillation, there remains a brown oil (impure hypobenzoylite of ethyl) which is insoluble in water, dissolves readily in alcohol and ether, is but slightly decomposed by aqueous potash, but readily by alcoholic potash,

with formation of small quantities of benzoate and hypobenzoylite of potash. If the alkaline solution be diluted with water and the alcohol separated from the clear liquid by distillation, hydrochloric acid then throws down from this liquid a mixture of benzoic and hypobenzoylous acids. This mixture is boiled with water, in which the hypobenzoylous acid is insoluble.

*Properties.* Yellowish brown; resinous; in the cold it has the consistence of thick turpentine, but melts very easily at the heat of the water-bath, into a transparent yellow liquid. The alcoholic solution reddens litmus slightly. The acid is not volatile.

| | | | Löwig & Weidmann. |
|---|---|---|---|
| 14 C | 84 | 76·37 | 76·67 |
| 6 H | 6 | 5·45 | 5·60 |
| 2½ O | 20 | 18·18 | 73 |
| | 110 | 100·00 | 100·00 |

At a higher temperature, it decomposes like the resins.—It appears to be oxidised by nitric acid.

It is insoluble in water, but dissolves very readily in alcoholic potash, forming a yellow solution whence it is precipitated by acids in its original state. The solution neutralised with acetic acid till it begins to be turbid, then filtered, and precipitated with acetate of lead, yields a yellowish white precipitate which, after drying at 100°, contains:

| | | | Löwig & Weidmann. |
|---|---|---|---|
| PbO | 112 | 52·58 | 52·90 |
| 14 C | 84 | 39·44 | 39·13 |
| 5 H | 5 | 2·35 | 2·93 |
| 1½ O | 12 | 5·63 | 5·04 |
| | 213 | 100·00 | 100·00 |

The solution of the acid in potash neutralised with nitric acid, forms with baryta or lime salts a yellowish precipitate; with ferric salts, a yellowish brown; with mercuric nitrate or chloride, a white; and with nitrate of silver, a yellow precipitate becoming brown when heated.

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## Sulphide of Benzylene.

$C^{14}H^{6},S^{2}$.

CAHOURS. (1848.) *N. Ann. Chim. Phys.* 23, 336; *J. pr. Chem.* 45, 133.

*Sulphobenzol.*

*Formation.* Produced by treating chloride of benzylene with an alcoholic solution of sulphide of hydrogen and potassium:

$$C^{14}H^{6}Cl^{2} + KS,HS = C^{14}H^{6}S^{2} + KCl + HCl.$$

White crystalline scales having a pearly lustre. Insoluble in water. Melts at 64° and solidifies in the crystalline state on cooling.

| | | | Cahours. |
|---|---|---|---|
| 14 C | 84 | 68·89 | 68·76 |
| 6 H | 6 | 4·92 | 4·97 |
| 2 S | 32 | 26·19 | 26·00 |
| $C^{14}H^{6}S^{2}$ | 122 | 100·00 | 99·73 |

The compound when strongly heated turns brown and volatilises, being at the same time partially decomposed. — It is violently attacked by nitric acid even when dilute, with formation of sulphuric acid and a substance which dissolves in alkalies and crystallises in yellow scales.

It dissolves sparingly in cold, readily in boiling alcohol, whence it crystallises in shining scales on cooling.

## Hydriodate of Benzylene.

$C^{14}H^{7}I = C^{14}H^{6},HI.$

CANNIZZARO. (1854.) Epistolary communication.

*Iodide of Benzyl, Hydriodwasserstoff-benzen.*

When a solution of benzylic alcohol (p. 19), in bisulphide of carbon is mixed with a saturated solution of phosphorus in bisulphide of carbon, iodine gradually added, and the sulphide of carbon distilled off after the action is terminated, there remains, besides iodide of phosphorus, a liquid which irritates the eyes strongly and probably consists of hydriodate of benzylene.

## Hydrochlorate of Benzylene.

$C^{14}H^{7}Cl = C^{14}H^{6},HCl.$

CANNIZZARO. (1853.) *Ann. Pharm.* 88, 130. — *N. Ann. Chim. Phys.* 45, 468; *Ann. Pharm.* 96, 246.

*Chloride of Benzyl, Chlorotoluene, Chlorwasserstoff-benzen, Ether benzhydrochlorique.*

*Preparation.* 1. When hydrochloric acid gas is passed through benzylic alcohol, the liquid becomes heated, assumes a brown colour, and divides into two layers. The upper layer is aqueous hydrochloric acid; the lower, which consists of impure hydrochlorate of benzylene, is removed, distilled in a current of dry hydrochloric acid gas, washed with carbonate of potash, dried by chloride of calcium, and rectified. — 2. Toluene, $C^{14}H^{8}$, is repeatedly distilled in a current of dry chlorine gas; and the product is washed with water and solution of potash, then

dehydrated by chloride of calcium, and repeatedly rectified. The liquid thus obtained, hitherto called chlorotoluene or chlorotoluol, is identical with the preceding.

*Properties.* Colourless, strongly refracting oil, heavier than water; and having a very pungent odour. Sp. gr. of (1) from 1·1136 to 1·1179, of (2) = 1·117. Boils between 175° and 176° (180° and 185° according to Cannizzaro's earlier statement).

Heated with alcoholic ammonia over the water-bath, it yields sal-ammoniac and a crystallised alkaloid which melts at a higher temperature then toluidine.—Heated with alcoholic potash, it yields chloride of potassium and benzylic alcohol.—Heated with an alcoholic solution of acetate of potash, it yields chloride of potassium and acetate of benzyl; and with alcoholic cyanide of potassium, it yields chloride of potassium and cyanide of benzyl.

Insoluble in water; dissolves readily in *alcohol* and *ether*.

## Chloride of Benzylene.

$C^{14}H^{6}Cl^{2} = C^{14}H^{6},Cl^{2}$.

CAHOURS. (1848.) *N. Ann. Chim. Phys.* 23, 329; *J. pr. Chem.* 46, 130; abstr. *Ann. Pharm.* 70, 329.

*Chlorobenzol.*

*Formation and Preparation.* Bitter almond oil and pentachloride of phosphorus act upon one another with great evolution of heat; and if the action is assisted by gentle heating, a mixture of two liquids passes over. One-fourth of the distillate boils between 108° and 112°, and consists of oxychloride of phosphorus; and when this is distilled off, and the residue mixed with water, chloride of benzylene separates in the form of an oil, which may be washed with dilute potash-ley and afterwards with pure water, then dried over chloride of calcium and distilled.

Colourless liquid, the odour of which is faint in the cold, but strongly penetrating at higher temperatures. Sp. gr. 1·245 at 16°. Boils between 206° and 208°. Vapour-density 5·595.

| | | | Cahours. |
|---|---|---|---|
| 14 C | 84·0 | 52·26 | 52·33 |
| 6 H | 6·0 | 3·72 | 3·72 |
| 2 Cl | 70·8 | 44·02 | 43·86 |
| $C^{14}H^{6}Cl^{2}$ | 160·8 | 100·00 | 99·91 |

| | Vol. | Density. |
|---|---|---|
| C-vapour | 14 | 5·8240 |
| H-gas | 6 | 0·4158 |
| Cl-gas | 2 | 4·9086 |
| Vapour | 2 | 11·1484 |
| | | 5·5742 |

It is not decomposed by potash, even with the aid of heat.

With an alcoholic solution of sulphide of hydrogen and potassium, it yields chloride of potassium and sulphide of benzylene.

It is insoluble in water, but dissolves readily in *alcohol* and *ether*.

## ¶. Cyanide of Benzyl.

$C^{16}NH^{7} = C^{2}N,C^{14}H^{7}$.

CANNIZZARO. *N. Ann. Chim. Phys.* 45, 468.

Obtained by boiling chloride of benzyl with a concentrated alcoholic solution of cyanide of potassium, till no more chloride of potassium separates from the liquid, and distilling the filtrate to remove the vinic alcohol. The residual liquid then separates into two layers, the upper containing cyanide of benzoyl, which may be obtained from it by rectification.

Colourless liquid which by boiling in strong caustic potash, is converted into toluic acid, $C^{16}H^{8}O^{4}$:

$$C^{16}NH^{7} + 4HO = C^{16}H^{8}O^{4} + NH^{3}. \quad ¶.$$

## Acetate of Benzyl.

$C^{18}H^{10}O^{4} = C^{14}H^{7}O,C^{4}H^{3}O^{3}$.

CANNIZZARO. (1853). *Ann. Pharm.* 88, 130.

*Essigbenzester, Ether benzacetique.*

*Preparation.* 1. When a solution of benzylic alcohol in 2 vol. acetic acid is mixed with a solution of 1 vol. oil of vitriol in 4 or 5 vol. acetic acid, the mixture becomes turbid after a short time, and an oily layer of acetate of benzyl forms on the surface of the liquid. This oil is removed, washed with a warm mixture of acetic acid and oil of vitriol, and afterwards with carbonate of potash, then dried over chloride of calcium, and rectified. — ¶. 2. Chloride of benzyl (prepared from toluol, p. 50) is boiled for two or three hours with a strong alcoholic solution of acetate of potash in an apparatus which allows the condensed vapours to flow back again; the precipitated chloride of potassium separated by filtration, and the greater part of the vinic alcohol removed from the filtrate by distillation. The remaining liquid then separates into two layers, the upper of which, when rectified yields acetate of benzyl. ¶.

Colourless oil, heavier than water, and having a very agreeable odour like that of pears. It boils at 210°.

Boiled with strong potash-ley, it yields acetate of potash and benzylic alcohol.

## Benzoate of Benzyl.

$C^{28}H^{12}O^4 = C^{14}H^7O,C^{14}H^5O^3$.

CANNIZZARO. (1854.) Epistolary communication.

*Benzylic Benzoate, Benzoe-benzester, Ether benzo-benzoique.*

When chloride of benzoyl and benzylic alcohol are distilled together in equal numbers of atoms, hydrochloric acid gas is evolved, and benzoate of benzyl distils over in the form of a yellowish oil. At the beginning of the distillation, small quantities of benzoic acid and hydrochlorate of benzylene likewise pass over, but at a later period, the benzoate of benzyl is obtained in a state of purity. The yellowish oil crystallises on cooling; the mass thus obtained is pressed between paper, and distilled over benzoic anhydride; and the distillate is washed with carbonate of potash and rectified. On cooling, crystals of benzoate of benzyl separate in the midst of the yellow liquid.

Colourless crystalline laminæ melting below 20°, into a colourless oil, which remains liquid long after it has been cooled below its melting point, and often requires the aid of a freezing mixture to crystallise it again. Boils a little below 345°.

| | | | Cannizzaro. |
|---|---|---|---|
| 28 C | 168 | 79·25 | 79·17 |
| 12 H | 12 | 5·67 | 5·84 |
| 4 O | 32 | 15·08 | 14·99 |
| $C^{28}H^{12}O^4$ | 212 | 100·00 | 100·00 |

The yellowish oil from which the benzoate of benzyl has crystallised, has the same composition as the crystals. The mixture boils between 340° and 345°, and consists of, 79·13 p. c. C, 5·94 H, and 14·93 O.

## Sulphobenzoic Acid.

$C^{14}H^6S^2O^{10} = C^{14}H^6O^4,2SO^3$.

MITSCHERLICH. (1834.) *Pogg.* 31, 287; further, *N. Ann. Chim. Phys.* 7, 5.
FEHLING. *Ann. Pharm.* 27, 222.

*Benzoeschwefelsäure, Benzoe-unterschwefelsäure.*

*Formation and Preparation.* — 1. When vapour of anhydrous sulphuric acid is passed over dry benzoic acid, or when solid anhydrous sulphuric acid is gradually mixed with dry benzoic acid, heat is evolved, and a viscid transparent mass is formed. If 2 pts. of benzoic acid are mixed with 1 pt. of anhydrous sulphuric acid, an additional portion of benzoic acid must be added after cooling, and the solid mass treated with water, which dissolves sulphobenzoic and excess of sulphuric acid, while benzoic acid separates out. The aqueous solution is saturated with car-

bonate of baryta, filtered, evaporated, and mixed while still hot with hydrochloric acid: acid sulphobenzoate of baryta then separates in crystals as the liquid cools. These crystals are purified by recrystallisation, and dissolved in water; the baryta precipitated by an exactly equivalent quantity of sulphuric acid; the sulphate of baryta separated by filtration; and the filtrate concentrated till it no longer boils at 150°. The acid is then obtained in the solid form on cooling. — 2. By the action of sulphuric acid on benzonitrile. (Buckton & Hofmann, xi, 156.) — 3. By the action of water on chlorosulphobenzoic acid. (Limpricht & v. Uslar, *Ann. Pharm.* 102, 252.)

$$C^{14}H^{4}Cl^{2}S^{2}O^{6} + 4HO = C^{14}H^{6}S^{2}O^{10} + 2HCl.$$

*Properties.* Solid crystalline mass which may be heated to 150° without decomposition; it deliquesces gradually in moist air, but recovers its solid form in a dry atmosphere.

*Decompositions.* — 1. By heating sulphobenzoic acid or any of its salts with excess of hydrate of potash till complete decomposition ensues, sulphite and sulphate of potash are produced. (Fehling.) — 2. The acid gently heated with pentachloride of phosphorus forms chlorosulphobenzoic acid, together with water and chlorophosphoric acid. (Limpricht & v. Uslar):

$$C^{14}H^{6}S^{2}O^{10} + PCl^{5} = C^{14}H^{4}Cl^{2}S^{2}O^{6} + 2HO + PCl^{3}O^{2}.$$

*Sulphobenzoates.*—Sulphobenzoic acid forms both neutral and acid salts ($C^{14}H^{4}M^{2}O^{4},2SO^{3}$ and $C^{14}H^{5}MO^{4}, 2SO^{3}$). — It decomposes nitrate and hydrochlorate of baryta, producing an acid baryta-salt.; it also decomposes hydrochlorate of ferric oxide. (Mitscherlich.) — According to Mitscherlich, the formula of the acid sulphobenzoates is $MO,C^{14}H^{5}O^{3},HO,SO^{3}$, and of the neutral salts: $MO,C^{14}H^{5}O^{3},SO^{3} + MO,SO^{3}$. Fehling has shown that the perfectly dried neutral salts contain 1 At. water less than this formula requires, and regards the acid as a conjugated hyposulphuric acid $= C^{14}H^{4}O^{3},S^{2}O^{5} + 2HO$. As it is difficult to explain on this hypothesis, why hyposulphuric acid, which is monobasic, should saturate 2 atoms of base, Berzelius supposes the acid to contain the copula $C^{14}H^{4}O^{2}$ united with $2SO^{3}$. (*Lehrb.* 5 Aufl. 4, 324.) — The bibasic nature of the acid finds a ready explanation in Gerhardt's law (vii. 222). According to this view, the formula of the acid is $C^{14}H^{6}O^{4},2SO^{3}$, and of the 6 atoms of hydrogen 2 At. are replaceable by metals.

*Sulphobenzoate of Potash.* — *a. Neutral.* — Obtained by double decomposition from neutral sulphobenzoate of baryta and neutral sulphate of potash. — Beautiful crystals which deliquesce in moist air. — *b. Acid.* — By decomposing acid sulphobenzoate of baryta with neutral sulphate of potash. — Beautiful efflorescent crystals. (Mitscherlich.)

*Sulphobenzoate of Baryta.* — *a. Neutral.* — The solution of the acid salt boiled with carbonate of baryta and evaporated, yields indistinct crystals, or generally mere crystalline crusts. The salt is very soluble in water. (Mitscherlich, Fehling.) It bears a very strong heat without decomposition, remaining unaltered even at the temperature of boiling oil. Deflagrates when suddenly heated with nitre or nitric acid. (Fehling.)

| | | | | Fehling. | Mitscherlich. | Buckton & Hofmann. |
|---|---|---|---|---|---|---|
| 2 BaO | 153·2 | 45·18 | 44·88 | | 43·68 | 45·31 |
| 14 C | 84·0 | 25·26 | 25·26 | | | |
| 4 H | 4·0 | 1·18 | 1·46 | | | |
| 2 O | 16·0 | 4·74 | 4·89 | | | |
| 2 $SO^3$ | 80·0 | 23·64 | 23·51 | | | |
| $C^{14}H^4Ba^2O^4,2SO^3$ | 337·2 | 100·00 | 100·00 | | | |

*b. Acid.* — *Preparation* p. *53*; also xi, 157. — Crystallises easily in oblique rhombic prisms belonging to the oblique prismatic system. $u : u = 82° 21'$; inclination of base to lateral edge = 98° 6′. The oblique lateral edge is generally truncated; mostly also the acute summit of this lateral edge; more rarely octohedral faces occur. The crystals are generally macled. (Fehling.) — Permanent in the air. Soluble in 20 pts. of water at 20°. The solution has an acid reaction. The crystals give off 9·13 p. c. (3 At.) water at 200°. (Mitscherlich.)

| | *Dry.* | | | Mitscherlich. | Buckton & Hofmann. | Limpricht & v. Uslar. |
|---|---|---|---|---|---|---|
| BaO | 76·6 | 28·27 | 28·36 | | 28·34 | 28·2 |
| 14 C | 84·0 | 31·22 | 31·40 | | | |
| 5 H | 5·0 | 1·85 | 1·86 | | | |
| 3 O | 24·0 | 8·92 | 8·66 | | | |
| 2 $SO^3$ | 80·0 | 29·74 | 29·72 | | | |
| $C^{14}H^5BaO^4,2SO^3$ | 269·6 | 100·00 | 100·00 | | | |

The salt is not decomposed by fuming nitric acid. (Mitscherlich.)

The acid sulphobenzoates of *magnesia, zinc-oxide, ferrous oxide, cobaltous oxide,* and *cupric oxide* yield fine crystals. (Mitscherlich.)

*Neutral Sulphobenzoate of Lead.* — Obtained by boiling the aqueous acid with excess of carbonate of lead. — Slender needles united in radiated groups; the solution in hot water solidifies almost completely on cooling. — The salt gives off 7·93 p. c. (4 At.) water at 220°. (Fehling.)

| | *Dry.* | | | Fehling. |
|---|---|---|---|---|
| 2 PbO | 224 | 54·89 | | 54·52 |
| 14 C | 84 | 20·58 | | 20·85 |
| 4 H | 4 | 0·98 | | 1·01 |
| 2 O | 16 | 3·91 | | 4·03 |
| 2 $SO^3$ | 80 | 19·64 | | 19·59 |
| $C^{14}H^4Pb^2O^4,2SO^3$ | 408 | 100·00 | | 100·00 |

*Neutral Sulphobenzoate of Silver.* — Crystallises in vacuo in small yellowish crystals which in drying give off 4·195 p. c. (2 At.) water. (Fehling.)

| | *Dry.* | | | Fehling. |
|---|---|---|---|---|
| 2 AgO | 232 | 55·77 | | 55·39 |
| 14 C | 84 | 20·19 | | 20·78 |
| 4 H | 4 | 0·96 | | 1·01 |
| 2 O | 16 | 3·85 | | 3·69 |
| 2 $SO^3$ | 80 | 19·23 | | 19·13 |
| $C^{14}H^4Ag^2O^4,2SO^3$ | 416 | 100·00 | | 100·00 |

## Benzoate of Methyl.

$C^{16}H^8O^4 = C^2H^3O,C^{14}H^5O^3$.

DUMAS & PELIGOT. (1835.) *Ann. Chim. Phys.* 58, 50.

*Benzoeformester, benzoesäures Methyloxyd, Benzoate de Methylène.*

*Preparation.* 1. A mixture of 1 pt. wood-spirit, 2 pts. benzoic acid and 2 pts. oil of vitriol is subjected to distillation; the residue again distilled two or three times with fresh wood-spirit; and the united distillates mixed with water. The impure benzoate of methyl which then sinks to the bottom is washed two or three times with water, agitated with chloride of calcium, decanted, and distilled over dry oxide of lead. — 2. Neutral sulphate of methyl is distilled with benzoate of potash or very dry benzoate of soda. — 3. Wood-spirit is distilled with oil of vitriol and hippurate of lime.

*Properties.* Colourless liquid of sp. gr. 1·10 at 17°, 1·0876 at 16·3° or 1·1026 at 0°. (H. Kopp.) — Boils at 198·5° when the barometer stands at 761 mm. (Dumas & Peligot); 199·2°, bar. at 746·4 mm. (H. Kopp, *Ann. Pharm.* 94, 307.) Vapour-density 4·717. Has an agreeable balsamic odour.

| | | | | Dumas & Peligot, *from hippuric acid.* |
|---|---|---|---|---|
| 16 C | 96 | 70·59 | 71·4 | 71·1 |
| 8 H | 8 | 5·88 | 6·2 | 6·0 |
| 4 O | 32 | 23·53 | 22·4 | 22·9 |
| $C^{16}H^8O^4$ | 136 | 100·00 | 100·0 | 100·0 |

| | Vol. | Density. |
|---|---|---|
| C-vapour | 16 | 6·6560 |
| H-gas | 8 | 0·5544 |
| O-gas | 2 | 2·2186 |
| Vapour of Benzoate of Methyl | 2 | 9·4290 |
| | 1 | 4·7145 |

*Decompositions.* 1. The vapour passed through a red-hot tube filled with lime yields benzol. Probably thus (Muspratt & Hofmann, *Ann. Pharm.* 54, 11):

$$C^{16}H^8O^4 = C^{12}H^6 + C^2H^2 + 2CO^2.$$

2. Benzoate of methyl absorbs chlorine gas without visible alteration; if however the saturated liquid be heated nearly to the boiling point, a large quantity of hydrochloric acid is given off, together with a little chloride of methyl; the residual liquid consists for the most part of chloride of benzoyl. Three-fourths of this liquid distils over at 194° or 195° and consists chiefly of chloride of benzoyl; the portion which distils below this temperature has no constant boiling point, yields hydrochloric, benzoic, and formic acids when decomposed by potash, and perhaps consists of chlorobenzoate of methyl. The residue left after the

distillate at 195° has passed over, is thick, black, and contains benzoic acid, benzoate of methyl, and perhaps chlorobenzoate of methyl. (Malaguti, *Ann. Chim. Phys.* 70, 387.)

## Mandelic Acid.

$C^{16}H^8O^6 = C^{14}H^6O^2,C^2H^2O^4$.

WINCKLER. (1835.) *Ann. Pharm.* 18, 310; *Pogg.* 41, 375; *Repert.* 57, 314.
LIEBIG. *Ann. Pharm.* 18, 319; *Pogg.* 41, 384.
LAURENT. *Ann. Chim. Phys.* 65, 202.
WÖHLER. *Ann. Pharm.* 66, 238.

*Formobenzoic acid, Formobenzoesäure, Acide formobenzoilique, Mandelsäure, Bittermandelolameisensäure.*

*Formation.* 1. By heating bitter almond water with hydrochloric acid. (Winckler.) The hydrocyanic acid is then resolved into ammonia and formic acid, which, at the moment of its formation, unites with the bitter almond oil (Liebig);—2. By the action of fuming sulphuric acid on bitter almond oil. (Laurent.)—3. By heating amygdalin with fuming hydrochloric acid. (Wöhler, *Ann. Pharm.* 66, 238.)

*Preparation.* Bitter almond water—obtained by distilling 80 oz. of bitter almond paste with 90 lbs. of water till 160 oz. have passed over, then taking 80 oz. of this liquid, and shaking up the distillate with the bitter almond oil—is mixed with 4 oz. of hydrochloric acid of sp. gr. 1·12, and evaporated to dryness over the water-bath, till all the hydrochloric acid is expelled. The yellowish crystalline residue smelling slightly of bitter almonds, leaves pure sal-ammoniac when treated with cold ether; and the ethereal solution yields by spontaneous evaporation, a slightly yellow crystalline mass, which, when treated with water, leaves a resinous flocculent body having the odour of bitter almonds. The aqueous solution is transparent and colourless, and contains pure mandelic acid which crystallises on evaporation. (Winckler.)—2. When bitter almond oil is treated with ⅛ of its volume of fuming sulphuric acid, heat is evolved, the liquid becomes brown and thick, and solidifies in a compact mass on cooling. The mass when treated with water yields an upper semi-solid layer containing undecomposed bitter almond oil and stilbylous acid, and a lower layer containing mandelic acid and excess of sulphuric acid: the mandelic acid crystallises from the latter on cooling. (Laurent.)—[3. A solution of amygdalin in hydrochloric acid is evaporated over the water-bath and the syrupy mass treated with ether, which dissolves the mandelic acid. On evaporating the solution, the mandelic acid crystallises. (Wöhler, Lg.)]

*Properties.* Scaly crystalline mass. (Winckler.) Crystallises sometimes in rhombic needles, sometimes in rhomboidal plates, frequently having their acute angles truncated (Laurent); in plates belonging to the rhombic system. (J. Heusser, *Pogg.* 94, 637.)—Has a very faint odour of sweet almonds, and a strong acid taste with a somewhat styptic aftertaste. Melts easily, with loss of water, into a yellow oil, which, on

cooling, solidifies to a translucent gum. (Winckler.) — When a solution of mandelic acid in strong hydrochloric acid is evaporated at a temperature above 100°, it becomes amorphous, and afterwards forms a solution with a small quantity of water, but is precipitated by a larger quantity in the form of a heavy yellowish oil. (Wöhler, *Ann. Pharm.* 66, 240.)

| | | | | Liebig. |
|---|---|---|---|---|
| 16 C | 96 | 63·15 | | 63·10 |
| 8 H | 8 | 5·26 | | 5·52 |
| 6 O | 48 | 31·59 | | 31·38 |
| $C^{16}H^{8}O^{6}$ | 152 | 100·00 | | 100·00 |

*Decompositions.* The acid heated above its melting point, diffuses an agreeable odour recalling those of white-thorn blossoms, hyacinth and gum benzoin. — Heated in a distillatory apparatus to a temperature short of carbonisation, it is converted into a dark brown, resinous, balsamic mass, which dissolves sparingly in water, but readily in alkalies and in alcohol. A large quantity of bitter almond oil passes over at the same time. — The acid burns with a red smoky flame, leaving a bulky, easily combustible charcoal. (Winckler.) — When it is boiled with *nitric acid* as long as *nitrous fumes* continue to escape, the formic acid is decomposed, and the bitter almond oil is converted into benzoic acid, which crystallises on addition of water. (Liebig.) — When *chlorine gas* is passed through an aqueous solution of mandelic acid, an oil smelling like chloride of benzoyl separates at first; and if potash be then added and the passage of the chlorine continued till this oil has completely disappeared, the solution, when subsequently treated with acid, gives off carbonic acid and deposits benzoic acid in the form of a crystalline magma. (Liebig.) — The acid dissolves in *oil of vitriol*, and the solution when gently heated, gives off carbonic oxide. (Liebig.) — The aqueous solution boiled with *peroxide of manganese* yields carbonic acid and bitter almond oil. (Liebig.)

*Combinations.* The acid is very soluble in water.

*Mandelates.* — The acid neutralises bases completely and expels carbonic acid from its compounds. (Winckler.)

*Mandelate of Ammonia.* — The aqueous acid is slightly supersaturated with ammonia and left to evaporate.—The salt is very difficult to crystallise, and generally forms a yellowish white mass. It has a very mild taste. When heated, it decomposes in the same manner as the free acid. — It dissolves in the smallest quantity of water and readily in alcohol. (Winckler.)

*Mandelate of Potash.* — Obtained by nearly neutralising carbonate of potash with the aqueous acid, so that the liquid retains a slight alkaline reaction, evaporating to dryness, exhausting the dry mass with alcohol, and leaving the alcoholic solution to evaporate. White, soft, easily friable, soapy mass, having a very mild, scarcely saline taste, faintly resembling that of sweet almonds. Decomposes like the free acid when heated, takes fire easily and burns away completely, leaving pure carbonate of potash. — Dissolves very readily in water and alcohol. (Winckler.)

*Mandelate of Baryta.* — Obtained by decomposing carbonate of baryta with mandelic acid.—20 pts. of the acid decompose 13·38 pts. of carbonate of baryta. (1 At. acid : 1 At. $BaO,CO^2$.) — The salt crystallises readily in small, tolerably hard needles. When heated, it behaves like the potash-salt. — It is much less soluble in water than the potash-salt. (Winckler.)

*Mandelate of Magnesia.* — Crystallises readily. (Winckler)

*Mandelate of Lead.* — Precipitated as a white, finely crystalline powder on adding mandelate of potash to neutral acetate of lead. When carefully heated in close vessels, it yields an oil which appears to be nearly pure bitter almond oil. Scarcely soluble in water. (Winckler.)

*Mandelate of Copper.* — A solution of sulphate of copper is precipitated by mandelate of potash. — Fine light blue powder. Behaves like the lead-salt when subjected to dry distillation. — Nearly insoluble in water and alcohol. (Winckler.)

| | | | | Liebig. | Winckler. |
|---|---|---|---|---|---|
| CuO | 40 | | 21·86 | | 21·5 |
| 16 C | 96 | | 52·46 | 52·41 | |
| 7 H | 7 | | 3·82 | 3·96 | |
| 5 O | 40 | | 21·86 | | |
| $C^{16}H^7CuO^6$ | 183 | | 100·00 | | |

*Mercuric Mandelate.* — Obtained by precipitating mercuric nitrate with mandelate of potash. — Its reactions closely resemble those of the copper salt. (Winckler.)

*Mandelate of Silver.* — Obtained by precipitating nitrate of silver with neutral mandelate of mercury. White, heavy, crystalline powder, easy to wash. Crystallises from its aqueous solution saturated at the boiling heat in rather hard crystals having a slight yellowish colour.

| | | | | Liebig. | Winckler. |
|---|---|---|---|---|---|
| AgO | 116 | | 44·82 | | 44·5 |
| 16 C | 96 | | 37·04 | 37·15 | |
| 7 H | 7 | | 2·70 | 2·87 | |
| 5 O | 40 | | 15·44 | | |
| $C^{16}H^7AgO^6$ | 259 | | 100·00 | | |

Melts at a somewhat high temperature into a dark mass, and yields the same products of decomposition as the acid, leaving metallic silver. (Winckler.)

Mandelic acid dissolves in the smallest quantities of *alcohol* and *ether*. (Winckler.)

pricht & List) yields nitrobenzoate of ethyl. When nitric acid alone is used, a considerable quantity of the compound ether is decomposed, and free nitrobenzoic acid is formed. (E. Kopp.) — 4. Benzoic ether treated with strong aqueous potash becomes thick and nearly solid; if water be then added, a portion dissolves, while the rest sinks to the bottom and disappears gradually. (Deville.) — The ether shaken up for some time with potash, disappears, the liquid then containing alcohol and benzoate of potash. (Scheele, Thénard.) — 5. When it is heated with a mixture of hydrate of potash and quick-lime, hydrogen is evolved, and benzoate and acetate of potash are produced. (Dumas & Stas, *Ann. Chim. Phys.* 73, 152.) — 6. *Sodium* does not act upon benzoic ether in the cold; the action begins at 60° or 70°, and is rather lively at 100°. The liquid turns brown, and yields, without evolution of gas, a solid mixture of hypobenzoylite of ethyl, and a small quantity of undecomposed benzoate of ethyl, together with benzoate of soda and ethylate of sodium. (Löwig & Weidmann, *Pogg.* 50, 105.) — Benzoic ether is not attacked by pentachloride of phosphorus. (Cahours.)

*Combinations.* 1. Benzoic ether is insoluble in cold, and sparingly soluble in hot water. — 2. It absorbs *ammoniacal gas*, forming a white mass, which is resolved by water into undecomposed benzoic ether and ammonia: acids accelerate this decomposition. (Deville.) — When left in contact for some time with aqueous ammonia, it forms benzamide. — 3. With *bichloride of tin* it forms a crystallisable compound, which is difficult to purify and very apt to decompose. (Löwig, *Compt. rend.* 21, 371.) — 4. It dissolves readily in *alcohol* and *ether*.

## 1. Sulphobenzoate of Ethyl.

$$C^{28}H^{14}S^{2}O^{10} = 2C^{4}H^{5}O,C^{14}H^{4}S^{2}O^{6}.$$

LIMPRICHT & V. USLAR. *Ann. Pharm.* 102, 252.

Absolute alcohol becomes strongly heated in contact with chlorosulphobenzoic acid $C^{14}H^{4}Cl^{2}S^{2}O^{6}$; hydrochloric acid and chloride of ethyl are given off; and on evaporating the liquid over the water-bath, sulphobenzoate of ethyl remains in the form of a syrupy residue having a faint ethereal odour. — It dissolves in water in all proportions, and cannot therefore be purified, like most compound ethers, by washing with water. On heating the aqueous solution, the ether is resolved into alcohol and sulphobenzoic acid. The ether cannot be distilled without decomposition; when heated in a retort, it leaves a large quantity of charcoal, swells up considerably, and yields a small quantity of distillate having a disagreeable odour. Treated with gaseous or aqueous ammonia, it yields ethylosulphobenzoate of ammonia.

## ¶. Ethylosulphobenzoic Acid.

$C^{18}H^{10}S^2O^{10} = C^4H^5O,HO,C^{14}H^4S^2O^8$.

LIMPRICHT & v. USLAR. *Ann. Pharm.* 102, 255.

*Sulphobenzovinic acid.*

Produced in the form of an ammonia-salt by dissolving chlorosulphobenzoic acid in alcoholic ammonia, or by dissolving sulphobenzoic ether in alcohol and passing ammonia through the solution. On evaporating the liquid, the ammonia-salt is obtained in crystals; and by dissolving these in water, precipitating the ammonia with bichloride of platinum, removing the excess of platinum by sulphuretted hydrogen, and evaporating the filtrate at the heat of the water-bath, ethylosulphobenzoic acid is obtained in the form of a yellowish syrup, which does not show any signs of crystallisation, even after standing for several days. The acid appears however to be crystallisable, but difficult to obtain in the crystalline form on account of its proneness to decomposition; for on decomposing the baryta-salt with an equivalent quantity of sulphuric acid, and evaporating the filtrate over the water-bath, a syrup was obtained which solidified in a crystalline mass on cooling, but on being saturated with carbonate of baryta, yielded a mixture of sulphobenzoate and ethylosulphobenzoate of baryta.

The *Ethylosulphobenzoates* are all very soluble: they are most readily prepared from the ammonia-salt by precipitating the ammonia with bichloride of platinum, removing the excess of platinum by sulphuretted hydrogen, and neutralizing the filtrate with the required base.

*Ethylosulphobenzoate of ammonia.* — (*Preparation, vid. sup.*). The solution when evaporated yields crystals to the last drop. The crystals are four-sided tables, very large and well-defined, especially when separated at a winter temperature, and have a very distinct cleavage parallel to the shorter side of the base. They melt at about 185°, into a transparent viscid mass, which does not solidify till cooled below 150°; if the heat be raised to 250° or above, the salt froths up strongly without blackening, and the residue left after the frothing has ceased, solidifies in a crystalline mass, which dissolves readily in water or alcohol, and crystallises therefrom in small nodular crystals, which give off ammonia when treated with potash, even in the cold; but if the heat is raised above 300°, complete decomposition takes place, water, benzonitrile, benzoic acid and sulphurous acid being given off, and a strongly tumefied charcoal remaining behind. The salt is decomposed by potash-ley even in the cold, with evolution of ammonia. Heated with aqueous potash to 100° for a few hours in a sealed tube, it is decomposed into sulphobenzoic acid, alcohol and ammonia.

| | | | Limpricht & v. Uslar (*mean*). |
|---|---|---|---|
| 18 C | 108 | 43·7 | 43·8 |
| 13 H | 13 | 5·2 | 5 6 |
| N | 14 | 5·6 | 5·8 |
| 2 S | 32 | 13·0 | 13·7 |
| 10 O | 80 | 32·5 | 31·1 |
| $C^{18}H^9(NH^4)S^2O^{10}$. | 247 | 100·0 | 100·0 |

The salt dissolves readily in water and alcohol, but is insoluble in ether. The solutions are neutral to test paper.

*Ethylosulphobenzoate of Soda.* — Prepared as above, or by mixing aqueous solution of the ammonia-salt with carbonate of soda, evaporating over oil of vitriol at a very gentle heat, boiling the dry residue with absolute alcohol and leaving the alcohol to evaporate. Milk-white needles united in nodules easily soluble in water and alcohol.

| | | | Limpricht & v. Uslar. |
|---|---|---|---|
| 18 C | 108 | 42·9 | 42·9 |
| 9 H | 9 | 3·5 | 3·7 |
| Na | 31 | 9·1 | 9·5 |
| 2 S | 32 | 12·7 | |
| 10 O | 80 | 31·8 | |
| $C^{18}H^{9}NaS^{2}O^{10}$ | 260 | 100·0 | |

The salt appears to contain 2 At. water of crystallisation, part of which is given off in drying over oil of vitriol. Two crops of crystals which had stood for several days over oil of vitriol, gave off 5·3 and 5·7 p.c. water at 100°. (2 At. = 6·6 per cent.)

*Ethylosulphobenzoate of Baryta,* crystallises after some time from a highly concentrated aqueous solution, in small, well defined, rhombic tables, which when left over oil of vitriol, give off their water of crystallisation and fall to pieces.

| | | | Limpricht & v. Uslar. |
|---|---|---|---|
| $C^{18}H^{9}S^{2}O^{10}$ | 227·0 | 77·2 | |
| Ba | 68·6 | 22·8 | 22·7 |
| $C^{18}H^{9}BaS^{2}O^{10}$ | 295·6 | 100·0 | |

*Ethylosulphobenzoate of Silver.* — By decomposing the baryta-salt with sulphate of silver and concentrating the filtrate at a gentle heat, the silver-salt is obtained in small transparent needles arranged in concentric groups. (Limpricht & v. Uslar.) ¶

## Benzoglycolic Acid.

$C^{18}H^{8}O^{6} = C^{14}H^{6}O^{3},C^{4}H^{2}O^{3}$.

Ad. Strecker. (1847.) *Ann. Pharm.* 68, 54.
N. Socoloff & Ad. Strecker. *Ann. Pharm.* 79, 369; 80, 18.
Gössmann. *Ann. Pharm.* 90, 181.

*Formation and Preparation.* 1. Dry hippuric acid is rubbed up to a thin paste with commercial nitric acid, and a current of nitric oxide gas

passed into the mixture, which is kept cold and frequently stirred; nitrogen gas is then evolved and the hippuric acid dissolves. When the liquid exhibits a green colour (which it does after five or six hours), part of the benzoglycolic acid is already separated in the crystalline state. The portion which still remains dissolved is for the most part precipitated by treating the liquid when cold with a large quantity of water. The yellowish crystalline mass obtained by filtering and washing out the acid liquid is suspended in water and neutralized with milk of lime, the paste, which is thin at first, then solidifying into a hard mass; the liquid obtained by heating is filtered while still hot; and, as the filtrate cools, the lime-salt crystallises in slender needles, which may be rendered colourless by washing with a small quantity of cold water, and pressure between paper. — The somewhat yellowish mother-liquor may be decolorised by animal charcoal, but generally contains a small quantity of benzoate of lime. — The acid liquid which has run off from the crude benzoglycolic acid still retains in solution a small quantity of that acid, which may be separated from it by neutralising it exactly with carbonate of potash, crystallising out the nitrate by repeated evaporation, and mixing the last mother-liquor with strong nitric acid. The benzoglycolic acid thus separated is generally contaminated with a large quantity of benzoic acid, which however may be removed by exactly neutralising one half of the mixture with lime, mixing it with the other half, evaporating to dryness, and extracting the benzoic acid from the residue by means of ether (being the stronger acid of the two, it remains in the free state); benzoglycolate of lime is then left undissolved. — By dissolving the lime-salt in water, and decomposing it with hydrochloric acid, pure benzoglycolic acid is obtained as a white crystalline powder; larger crystals are obtained by dissolving the lime-salt in alcohol, decomposing it with sulphuric acid, filtering from the gypsum, and leaving the filtrate to evaporate. (Socoloff & Strecker.)

2. Hippuric acid is dissolved in excess of moderately dilute potash-ley, and chlorine gas passed slowly through the liquid, which, as soon as the evolution of nitrogen gas is terminated, is carefully neutralised with hydrochloric acid, then concentrated by the application of a gentle heat, and mixed with a slight excess of hydrochloric acid; the solution then solidifies in a crystalline mass. If the liquid be kept warm, the benzoglycolic acid separates in yellow oily drops which solidify in the crystalline form on cooling. For purification, the acid is dissolved in ether, and the ether carefully distilled off from the watery layer below it; the acid then separates as in oil, in the midst of the water. (Gössmann.)

*Properties.* Prisms of 37° 40′ and 142° 20′, frequently taking the form of thin plates.—Melts when heated and solidifies in the crystalline form.

| | | | Socoloff & Strecker. |
|---|---|---|---|
| 18 C | 108 | 60·00 | 60·09 |
| 8 H | 8 | 4·44 | 4·66 |
| 8 O | 64 | 35·56 | 35·25 |
| $C^{18}H^{8}O^{8}$ | 180 | 100·00 | 100·00 |

*Decompositions.* The acid when boiled for some time with water, is gradually resolved into glycolic and benzoic acids:

$$C^{18}H^{8}O^{8} + 2HO = C^{14}H^{6}O^{4} + C^{4}H^{4}O^{6}.$$

A more rapid decomposition is effected by boiling the acid with water containing a little sulphuric acid. (vid. *Glycolic* acid,) — 2. Benzoglycolic acid heated above its melting point gives off vapours containing benzoic acid, which excite coughing, and leaves a small quantity of easily combustible charcoal.

*Combinations. a.* The acid dissolves very sparingly in cold, more readily in hot water. When boiled with a quantity of water not sufficient to dissolve it, it melts into oily drops.

*b. Benzoglycolates.* — The acid neutralises bases completely. The salts have a faint but peculiar taste. They are for the most part soluble in water, many also in alcohol. From the greater number of them, the benzoglycolic acid is separated in the crystalline form on the addition of stronger acids. They may be boiled with water for a long time without perceptible decomposition.

*Benzoglycolate of Ammonia.* — Obtained by saturating the acid with ammonia, or by decomposing the lime-salt with carbonate of ammonia. — Gives off ammonia when evaporated.

*Benzoglycolate of Potash.* — Prepared like the ammonia-salt. — Very easily soluble in water and alcohol. By spontaneous evaporation it forms cauliflower-like masses. From a hot-saturated solution it crystallises in broad, very thin plates, on cooling.

*Benzoglycolate of Soda.* — Crystallises more readily than the potash-salt; from a hot saturated solution, it separates on cooling in rather large rhombic tables. At 100° it gives off 21·08 p. c. (6 At.) water, and becomes opaque, but retains its lustre.

| | *At* 100°. | | | Socoloff & Strecker. |
|---|---|---|---|---|
| NaO | 31·2 | .... | 15·43 | ..... 15·42 |
| $C^{18}H^{7}O^{7}$ | 171·0 | .... | 84·57 | |
| $C^{18}H^{7}NaO^{8}$ | 202·2 | .... | 100·00 | |

*Benzoglycolate of Baryta.* — Delicate silky needles, which give off 6·69 p. c. (2 At.) water at 100°.

| | | | | Socoloff & Strecker. |
|---|---|---|---|---|
| BaO | 76·6 | .... | 30·94 | ..... 30·92 |
| $C^{18}H^{7}O^{7}$ | 171·0 | .... | 69·06 | |
| $C^{18}H^{7}BaO^{8}$ | 247·6 | .... | 100·00 | |

*Benzoglycolate of Lime.* — Obtained by saturating the acid with milk of lime (p. 65). — Delicate silky needles, united in concentric groups.

| | *Crystallised.* | | | Socoloff & Strecker. |
|---|---|---|---|---|
| CaO | 28 | | 13·46 | 13·33 |
| 18 C | 108 | | 51·92 | 52·03 |
| 8 H | 8 | | 3·85 | 4·16 |
| 8 O | 64 | | 30·77 | 30·48 |
| $C^{18}H^{7}CaO^{8}$ + Aq | 208 | | 100·00 | 100·00 |

The crystallised salt gives off 4·24 p. c. (1 At.) water at 120°. — It dissolves in 43·32 pts. of water at 11° and in 7·54 pts. at 100°. The solution saturated at the boiling heat often deposits but a small quantity of salt on cooling, but if it be then strained, it becomes turbid, and in a few seconds solidifies to a thick jelly; if the liquid be then filtered, the mother-liquor generally solidifies a second time.

*Benzoglycolate of Magnesia.* — Prepared by mixing the boiling solutions of sulphate of magnesia and benzoglycolate of lime, and exhausting with alcohol the solid mass which forms on cooling. Long, very slender needles.

*Benzoglycolate of Zinc.* — A solution of the lime-salt saturated at the boiling heat, and mixed with chloride of zinc, yields on cooling, long thin needles, which completely fill the vessel; they are separated by filtration, washed with water, pressed between paper and recrystallised. — The crystals give off 14·71 p. c. (4 At.) water at 100°.

| | *At* 100°. | | | Socoloff & Strecker. |
|---|---|---|---|---|
| ZnO | 40·6 | | 19·19 | 19·42 |
| $C^{18}H^{7}O^{7}$ | 171·0 | | 80·81 | |
| $C^{18}H^{7}ZnO^{8}$ | 211·6 | | 100·00 | |

*Benzoglycolate of Lead.* — *a. Sexbasic.* — When the cold solution of the lime-salt is precipitated by basic acetate of lead, the precipitate partially washed, then immersed in cold water, and the liquid filtered, the filtrate yields after a while, short slender needles united in stellate groups; they may be freed from adhering carbonate of lead by elutriation. — The crystals give off 2·63 p. c. (2 At.) water at 100°.

| | *At* 100°. | | | Socoloff & Strecker. |
|---|---|---|---|---|
| 6 PbO | 672 | | 79·72 | 79·71 |
| $C^{18}H^{7}O^{7}$ | 171 | | 20·28 | |
| $C^{18}H^{7}PbO^{8},5PbO$ | 843 | | 100·00 | |

The precipitate obtained by mixing a boiling solution of the lime salt with neutral acetate of lead, is a mixture of several basic salts containing 75·6 per cent. of oxide of lead.

*b. Sesquibasic.* — The cold aqueous solution of the lime-salt forms with solution of neutral acetate of lead, an abundant, curdy, flocculent precipitate which dissolves sparingly in cold water, and when boiled with water, first melts and then dissolves in it completely; the liquid, yields on cooling, first an amorphous deposit and afterwards crystals. When the original precipitate is covered with a quantity of cold water sufficient to dissolve it completely, and the solution filtered, the sesquibasic salt separates at first in hemispherical groups of crystals which melt at 100°, giving off 3·83 p. c. (6 At.) water.

| | | | Socoloff & Strecker. |
|---|---|---|---|
| 3 PbO | 336 | 49·56 | 49·29 |
| 2 $C^{18}H^{7}O^{7}$ | 342 | 50·44 | |
| $2C^{18}H^{7}PbO^{7},3PbO$. | 678 | 100·00 | |

*c. Monobasic.* — The mother-liquor of *b*, after standing for some time, deposits the neutral salt in crystals which resemble those of the salt *a*, and melt with partial decomposition at 100°.

| | *At* 100°. | | Socoloff & Strecker. |
|---|---|---|---|
| PbO | 112 | 39·58 | 39·27 |
| $C^{18}H^{7}O^{7}$ | 171 | 60·42 | |
| $C^{18}H^{7}PbO^{8}$ | 283 | 100·00 | |

*Ferric Benzoglycolate.* — The solution of the lime-salt yields with ferric hydrochlorate, a flesh-coloured precipitate insoluble in water, which becomes darker on the surface when dried. After drying in the air, it gives off 27·36 p. c. (28 At.) water at 100°.

| | *At* 100°. | | Socoloff & Strecker. |
|---|---|---|---|
| 2 $Fe^{2}O^{3}$ | 156 | 23·32 | 23·27 |
| 3 $C^{18}H^{7}O^{7}$ | 513 | 76·68 | |
| 2 $Fe^{2}O^{3},3C^{18}H^{7}O^{7}$ | 669 | 100·00 | |

*Benzoglycolate of Copper.* — A boiling saturated solution of the lime-salt, mixed with nitrate of copper, yields on cooling an abundant crop of blue rhombic tables, which may be washed with cold water and recrystallised. The crystals become green and opaque at 100°, but retain their lustre; they dissolve sparingly in cold, somewhat more readily in warm water; when they are heated with a quantity of water not sufficient to dissolve them, the undissolved portion forms a green powder, probably consisting of anhydrous salt.

*Benzoglycolate of Silver.* — The neutral ammonia-salt is precipitated by nitrate of silver, and the precipitate washed with very cold water and recrystallised from boiling water.

White microscopic crystals which quickly blacken in the light when moist; they dissolve sparingly in cold, readily in boiling water.

| | | | Socoloff & Strecker. |
|---|---|---|---|
| 18 C | 108 | 37·63 | 37·76 |
| 7 H | 7 | 2·44 | 2·57 |
| Ag | 108 | 37·63 | 37·64 |
| 8 O | 64 | 22·30 | 22·03 |
| $C^{18}H^{7}AgO^{8}$ | 287 | 100·00 | 100·00 |

Benzoglycolic acid dissolves readily in *alcohol* and *ether*.

The alcoholic solution of benzoglycolic acid gives off a peculiar odour when left to stand for some time. An alcoholic solution of benzoglyco-

late of lime, in which an additional quantity of lime-salt is suspended, yields, when hydrochloric acid gas is passed into it, not benzoglycolic but benzoic ether.

## Hippuric Acid.

$C^{18}NH^9O^6 = C^{18}AdH^7O^6$.

FOURCROY & VAUQUELIN. (1799.) *A. Tr.* 6, 197, 87, 199.—*Scher. J.* 2, 432.—Further *Ann. Chim.* 69.
LIEBIG. (1830.) *Pogg.* 17, 389; also *Br. Arch.* 34, 237;—*Ann. Pharm.* 12, 20.
DUMAS & PELIGOT. *Ann. Chim. Phys.* 57, 327; *Ann. Pharm.* 14, 69.
MITSCHERLICH. *Pogg.* 33, 335.
PELOUZE. *Ann. Pharm.* 26, 60; also *J. pr. Chem.* 13, 420.
FEHLING. *Ann. Pharm.* 28, 48.
URE. *J. Pharm.* 27, 646.—*J. Chem. Méd.* 17, 648.—*Repert.* 75, 61.
SCHWARZ. *Ann. Pharm.* 54, 29; 75, 195.
DESSAIGNES. *Compt. rend.* 21, 1224; *N. Ann. Chim. Phys.* 17, 15; *J. pr. Chem.* 37, 244.

*Hippursäure, Urinsäure, Pferdeharnsäure, Acide hippurique.*—Discovered in horse-urine, by Fourcroy & Vauquelin, but mistaken for uric acid; recognised as a distinct substance by Liebig.

*Sources.* In the urine: *a.* Of *man,*—in small quantity only, under normal conditions (Liebig, *Ann. Pharm.* 37, 82); abundantly in diabetes (100 pts. of urine yielded 0·025 of crystallised hippuric acid: Lehmann, *J. pr. Chem.* 8, 552; Hüngeld, *J. pr. Chem.* 8, 552); the urine of a girl thirteen years old, whose food consisted of apples with a little bread and water, contained as much hippuric acid as that of herbivorous animals. (Pettenkofer, *Ann. Pharm.* 53, 86.)—Respecting the occurrence of hippuric acid in human urine, see also Duchek (Schmidt's *Jahrb. d. ges. Med.* 84, 8).—*b.* Of *horses,* especially when worked but not overworked. (Liebig, *Thierchemié,* 3 Aufl. s. 86.) Riding-horses yield abundance of hippuric acid; agricultural horses yield benzoic acid (Erdmann & Marchand, *J. pr. Chem.* 26, 492); the urine of riding-horses which had before contained only hippuric acid, yielded benzoic acid, when they were put to harder work (Hulstein, *N. Br. Arch.* 66, 274); hippuric acid is present in the urine of horses when they are fed on oats and hay, not when they are fed on barley and straw. (Landerer, *N. J. Pharm.* 20, 288.)—*c.* Of *oxen,*—only when they are fed on distillery refuse (Schwarz, *Ann. Pharm.* 54, 31);—*d.* Of *camels,*—in large quantity (Schwarz);—*e.* Of *elephants.*—In guano (E. Marchand, *N. J. Pharm.* 7, 134); in the excrements of the caterpillars of butterflies and hawk-moths, and also in those of the insects themselves (J. Davy, *N. Ed. Phil. J.* 45, 17); in ox-blood (Verdeil & Dolfus, *Ann. Pharm.* 74, 215); in the scales formed in ichthyosis (Schlossberger, *Ann. Pharm.* 90, 378).

*Formation.* 1. The compound of glycocol with oxide of zinc placed together with chloride of benzoyl in a close vessel, yields hippuric acid

and chloride of zinc, slowly at ordinary temperatures, more quickly at 120°. (Dessaignes, *Compt. rend.* 37, 492):

$$C^4NH^5O^4,ZnO + C^{14}H^5ClO^2 = C^{18}NH^9O^6 + ZnCl + HO.$$

Hippuric acid is also obtained by heating glycocol with benzoic acid in a sealed tube. If the action be continued for 12 days at 160°, and the contents of the tube then treated with hot water, a solution is obtained which on cooling deposits three-fourths of the original quantity of benzoic acid; and the mother-liquor when concentrated yields hippuric acid in long prisms together with an additional quantity of benzoic acid. The water leaves undissolved a fine white tasteless powder, partly soluble in potash. (Dessaignes, *N. J. Pharm.* 32, 44.)

2. Benzoic acid is converted into hippuric acid in the animal organism. — The crystals resembling nitre found some time ago in the urine of a dog which had swallowed half a drachm of benzoic acid, were probably hippuric acid. (Wöhler, *Berzelius Lehrb.* 4 Aufl. Bd. iv. 376.) Urine voided two hours after swallowing benzoic acid or a soluble benzoate does not contain uric acid, but when mixed with $\frac{1}{12}$ of hydrochloric acid and evaporated, yields crystals of hippuric acid, which when mixed with dilute nitric acid and evaporated to dryness, produces a fine red purple colour with ammonia. (Al. Ure, *Repert.* 75, 61; further, *J. Pharm.* 27, 646.) Keller, before going to sleep, took 2 grammes of benzoic acid; the urine voided in the morning had an uncommonly strong acid reaction, and yielded crystals of hippuric acid when mixed with hydrochloric acid after concentration, and moreover contained urea and uric acid in normal proportion. (*Ann. Pharm.* 43, 198; compare H. Schwarz, *Ann. Pharm.* 54, 32.) A. B. Garrod found hippuric acid in his urine after taking between 20 and 30 grains of benzoic acid. The crystals of hippuric acid were mixed with granules of uric acid, which remained undissolved when treated with alcohol. The hippuric acid obtained from the alcoholic solution did not give with nitric acid and ammonia the reaction observed by Ure; the urine contained as much uric acid as when no benzoic acid was taken. (*Phil. Mag. J.* 20, 501; *J. pr. Chem.* 27, 356.) — Marchand, after taking 30 grains of benzoic acid, found 39·2 grains of hippuric acid in his urine. The benzoic acid must have taken up carbon, as otherwise it could only have yielded 34·23 grains of hippuric acid. If $C^4NH^5O^2$ were added to the benzoic acid, 30 grains of the latter would yield 44·01 grains of hippuric acid. (*J. pr. Chem.* 35, 309.)

*Preparation.* A. *From horses' or cows' urine.* — Horse-urine supersaturated with hydrochloric acid yields, after a while, a yellowish brown precipitate of impure hippuric acid. (Liebig, *Pogg.* 17, 389.) — Horse-urine mixed with hydrochloric acid, seldom yields hippuric acid without evaporation; hence it should be evaporated to $\frac{1}{6}$ or $\frac{1}{8}$, then mixed with hydrochloric acid and the crystallised hippuric acid purified. (Schwarz, *Ann. Pharm.* 54, 29; see also Dessaignes, *N. J. Pharm.* 32, 45.) — 100 pts. of cows' urine mixed with 2 or 3 pts. of crude hydrochloric acid, deposit hippuric acid. (Riley, *Chem. Soc. Qu. J.* 5, 97; *N. J. Pharm.* 22, 354.) — 2. The fresh urine of horses or cows is immediately mixed with excess of milk of lime; boiled for a few minutes; strained; the filtrate evaporated to $\frac{1}{6}$ or $\frac{1}{12}$, according to the degree of concentration, and supersaturated with hydrochloric acid. (Gregory.) Fresh cows' urine is mixed with hydrate of lime; boiled up once, decanted from the lime, and evaporated to $\frac{1}{8}$, then supersaturated with hydrochloric acid when cold, and the hippuric acid collected after 12 hours. If the

boiling with milk of lime be longer continued, a brown, resinous body is produced which greatly interferes with the purification of the hippuric acid. (Städeler, *Ann. Pharm.* 77, 18.) — 3. Fresh horse-urine is mixed with excess of sulphate of zinc; the liquid together with the resulting precipitate evaporated to $\frac{1}{6}$ or $\frac{1}{8}$ of the original bulk, filtered quickly, the residue washed with a small quantity of hot water, and the hippurate of zinc in the filtrate decomposed by means of dilute hydrochloric or sulphuric acid. Hippuric acid then separates in the form of a white magma, which may be washed with cold water, pressed between filtering paper, and recrystallised. (J. Löwe, *J. pr. Chem.* 65, 372.)

Hippuric acid separated by hydrochloric acid has a brownish colour and disagreeable urinary odour, and therefore requires further purification: *a.* The solution is boiled with quick lime; the filtrate mixed at the boiling heat with chloride of lime till the urinary odour is destroyed; animal charcoal then added till the liquid becomes colourless; and the filtrate is mixed with hydrochloric acid and left to cool. (Liebig, *Pogg.* 17, 389.) — The urine evaporated to a syrup is mixed with an equal volume of crude hydrochloric acid, chlorate of potash added till the liquid becomes colourless, and the solution left to cool. The chlorate of potash merely decomposes the resin and extractive matters. (Rieckher, *Jahrb. pr. Pharm.* 10, 244.) — The method of purification with chloride of lime (or hydrochloric acid and chlorate of potash) must be rejected, because a portion of the hippuric acid is thereby converted into benzoic acid. (Dumas & Peligot, Schwarz.) — *b.* The crude hippuric acid is once recrystallised, dissolved in caustic soda, and the solution while boiling hot mixed with successive small portions of manganate of potash, till a filtered sample dropped into excess of hydrochloric acid produces a pure white precipitate; the liquid is then filtered and the pure hippuric acid precipitated by addition of hydrochloric acid. (Gössmann, *Ann. Pharm.* 99, 373.) [Is not this method open to the same objection as the preceding? W.] — *c.* The crude acid is pressed, mixed with 10 pts. of boiling water and excess of milk of lime; the strained and expressed liquid mixed with solution of alum till the alkaline reaction disappears, and left to cool to 40°; carbonate of soda added as long as a precipitate is formed; and the solution strained, pressed, and precipitated by hydrochloric acid. The precipitated hippuric acid is washed with water, pressed, and dissolved in boiling water; blood-charcoal added (1 oz. to a pound of hippuric acid); and the solution filtered through paper while still at the boiling heat. (Bensch, *Ann. Pharm.* 58, 267.) — *d.* The crude acid is boiled with milk of lime, the greater part of the fibrin then going down with the precipitate; the filtrate precipitated with excess of carbonate of soda, boiled, filtered again, and precipitated with chloride of calcium, the carbonate of lime as it falls down carrying the colouring matter with it, — then filtered a third time, and precipitated with hydrochloric acid. (Schwarz, *Ann. Pharm.* 54, 29.) — *e.* The crude acid is suspended in an equal quantity of water, mixed with $\frac{1}{6}$ of nitric acid of sp. gr. 1·3, filtered after 24 hours and washed with cold water. (Hutstein, *N. Br. Arch.* 66, 274. — *f.* The crude acid dissolved in a large quantity of water is boiled for some time with finely divided zinc; a small quantity of recently ignited animal charcoal added to the boiling liquid as soon as the action upon the zinc becomes weak; and the liquid filtered into dilute hydrochloric or sulphuric acid. For purifying considerable quantities of hippuric acid, the crude acid dissolved in the smallest possible quantity of water, is neutralised with carbonate of soda, a slight excess of sulphate of zinc added; the liquid boiled for a short time with animal charcoal, and then

filtered into dilute sulphuric acid. (Löwe.) — [From admixed benzoic acid, crystallised hippuric acid is purified by pouring a little water on the mixture, adding ether and agitating, whereby the benzoic acid is completely dissolved. (Liebig.)]

B. From *human urine*. — The fresh urine is evaporated to a syrup over the water bath, mixed with a small quantity of hydrochloric acid, and shaken up with an equal volume of ether, which dissolves the hippuric acid. If the ethereal solution does not separate in the course of an hour, a quantity of alcohol $=\frac{1}{10}$ of the bulk of the mixture should be added: the liquid then immediately divides into two layers. The upper liquid, in addition to the hippuric acid, contains a small quantity of urea dissolved by the alcohol; it is therefore shaken up with a little water, which takes up the alcohol and the urea, while the hippuric acid remains dissolved in the ether. The hippuric acid which crystallises as the ether evaporates, is coloured yellowish or brown by a resinous substance, which however is easily removed by a little blood-charcoal. (Liebig, *Ann. Pharm.* 50, 170.)

*Properties*. Long, transparent, colourless or milk-white prisms, belonging to the right prismatic system. Cleavage parallel to the *p*-faces, $u'$, $u$, $y$ and $i$; $u : u' = 80° 8'$; $u' : u = 99° 52$; $i : u = 214° 49'$ (Dauber, *Ann. Pharm.* 74. 202); $u : u' = 80° 1'$; $u' : u = 99° 59'$; $i : i = 98° 30'$; $y : y = 88° 30'$; $i : u = 114° 49'$; $y : u = 123° 15'$. (Schabus *Wien. Akad. Ber.* 1850, 2, 211.) The ratio of the axes is 1 : 0·9760 : 1·1605 (Dauber); = 1 : 0·97442 : 1·2606. (Schabus.) — Reinsch, by spontaneous evaporation of the solution, obtained crystals resembling octohedrons. (*Jahrb. pr. Pharm.* 20, 217.) — The crystals have an unctuous diamond lustre. Sp. gr. 1·308. (Schabus.) In preparing hippuric ether from hippuric acid and alcohol, Liebig observed hippuric acid in cauliflower-like masses. Schwarz (*Ann. Pharm.* 75, 101) in preparing hippuric ether observed the same kind of masses to form in the mother-liquor; they separated unaltered from their hot aqueous solution, but on dissolving them in ammonia and adding hydrochloric acid, the hippuric acid was precipitated in the crystalline form. — The acid melts when heated, and solidifies in the crystalline form. It reddens litmus slightly, but does not taste sour.

| | | | Liebig. | Dumas & Peligot. | Mitscherlich. | Liebig, *from human urine.* | Schwarz, *amorphous.* |
|---|---|---|---|---|---|---|---|
| 18 C | 108 | 60·74 | 60·69 | 60·5 | 60·63 | 59·47 | 60·36 |
| N | 14 | 7·82 | 7·42 | 7·7 | 7·90 | | 7·88 |
| 9 H | 9 | 4·96 | 5·09 | 5·0 | 4·98 | 5·15 | 5·35 |
| 6 O | 48 | 26·48 | 26·80 | 26·8 | 26·49 | | 26·41 |
| $C^{18}NH^{9}O^{6}$ | 179 | 100·00 | 100·00 | 100·0 | 100·00 | | 100·00 |

Pelouze regards hippuric acid as a compound of bitter almond oil, hydrocyanic acid and formic acid:

$$C^{18}NH^{9}O^{6} = C^{14}H^{6}O^{2} + C^{2}NH + C^{2}H^{2}O^{4},$$

because, when subjected to dry distillation or boiled with peroxide of manganese and sulphuric acid, it yields carbonic acid, benzoic acid and ammonia. On the other hand, Socoloff & Strecker remark, that other compounds containing formic acid in conjunction with an aldide, yield

the aldide itself under these circumstances: *e. g.* mandelic acid (p. 58). — As hippuric acid when boiled with water and peroxide of lead, is resolved into benzamide and carbonic acid, Fehling regards it as benzamide conjugated with fumaric acid:

$$2C^{18}NH^9O^6 = 2C^{14}NH^7O^2 + C^8H^4O^8,$$

with regard to which view, Socoloff and Strecker observe that fumaric acid boiled with peroxide of lead does not yield carbonic acid. — From the decomposition of hippuric acid into benzoic acid and glycocol, Dessaignes concludes that it is a compound of anhydrous benzoic acid with anhydrous glycocol (analogous to sulphosaccharic acid, ix, 251): ($C^{18}NH^9O^6 = C^4NH^4O^2, C^{14}H^5O^2$), a view which appears also to be supported by the formation of hippuric acid from chloride of benzoyl and the compound of glycocol with oxide of zinc; but then, as Berzelius remarks, the decomposition by peroxide of lead cannot be explained. — H. Schwarz (*Ann. Pharm.* 75. 210) supposes that hippuric acid contains benzil and glycocol:

$$2C^{18}NH^9O^6 = C^{28}H^5O^4 + 2C^4NH^5O^4.$$

According to Socoloff & Strecker, hippuric acid is the amide of benzoglycolic acid, since, when treated with nitrous acid it behaves like other amides, yielding benzoglycolic acid. It is distinguished from most amidogen-acids by the fact that it is the amide of a monobasic acid, just as, for example, anthranilic acid is the amide of monobasic salicylic acid. (*Ann. Pharm.* 80, 17; compare Heintz, *Zoochemie S.* 283.)

*Decompositions.* 1. The acid blackens when heated, yields a crystalline sublimate of benzoic acid and benzoate of ammonia smelling strongly of benzoin, emits at the same time a powerful odour of hydrocyanic acid, and leaves a large quantity of porous charcoal. (Liebig.) — Heated in a retort, it yields at 210° a deposit of benzoic acid, and boils at 240°, giving off red-coloured benzoic acid, at the same time that hydrocyanic acid is evolved and benzonitrile distils over. In the retort there remains a resinous body, which is brittle in the cold, becomes soft when heated, is sparingly soluble in water, but dissolves readily in alcohol and ether. (Limpricht & v. Uslar, *Ann. Pharm.* 88, 133.) — Dry hippuric acid heated in a retort with quartz-sand and dried chloride of zinc yields benzonitrile, carbonic acid and charcoal. (Gösmann, *Ann. Pharm.* 100, 69.)

$$[C^{18}NH^9O^6 - 4HO = C^{14}NH^5 + CO^2 + 3C.]$$

2. Pure hippuric acid may be boiled for several days with water without undergoing any alteration. (Städeler.) — When horse-urine is very quickly evaporated, an odour of ammonia is evolved, and the urine is found to contain benzoic acid. (Fehling.) — When the urine is boiled by itself, the hippuric acid is readily converted into benzoic acid. (Dumas & Peligot, Gregory.) Cows' urine rapidly boiled does not yield benzoic acid. (Städeler.) — 3. Hippuric acid boiled for half an hour with excess of *potash* or *soda* yields glycocol and a benzoate of the alkali. (Dessaignes.) It is not decomposed by boiling with milk of lime. (Gregory, Schwartz.) — 4. From hot concentrated *hydrochloric acid*, hippuric acid crystallises without alteration (Liebig); but by continued

boiling it is completely resolved into benzoic acid and glycocol; the same decomposition is induced by *oil of vitriol* diluted with 2 pts. of water; by 20 minutes' boiling with *nitric acid*, benzoic acid and nitro-saccharic acid are produced: *oxalic acid* boiled for two hours with a very strong solution of hippuric acid, converts this acid into benzoic acid, the mother-liquor containing oxalo-saccharic acid. (Dessaignes.) This transformation is not attended with evolution of gas; 100 pts. of hippuric acid boiled with hydrochloric acid, yield 67·49 pts. of benzoic and 59·08 of hydrochloro-saccharic acid. (Calculation requires 68·15 benzoic and 62·09 hydrochloro-saccharic acid.) When 1 pt. of hippuric acid is boiled with a solution of 2 pts. chloride of zinc in an equal weight of water, benzoic acid sublimes and glycocol remains behind, mixed however with a small quantity of benzoate of zinc, resulting from the decomposition of the chloride by boiling. — 5. A solution of hippuric acid in cold nitric acid, is converted by *nitrous acid* into benzoglycolic acid, nitrogen gas and water:

$$C^{18}NH^{9}O^{6} + NO^{3} = C^{18}H^{8}O^{8} + 2N + HO.$$

Hippuric acid is not decomposed by boiling with nitrite of potash, because it does not set free the nitrous acid. — Hippuric acid in the state of cold aqueous solution is not decomposed by nitrous acid: but on the application of heat, nitrogen and hyponitric acid are evolved; and the latter produces further decomposition. The solution of hippuric acid in oil of vitriol is not decomposed by nitrous acid. (Socoloff & Strecker.) — 6. In a cold mixture of oil of vitriol and fuming nitric acid, hippuric acid is converted into nitrohippuric acid. (Bertagnini.) — 7. When the solution of hippuric acid *in oil of vitriol* is heated above 120°, it blackens, benzoic acid sublimes, and sulphurous acid is evolved. If the heat be discontinued when the sulphurous acid begins to go off and the black mass be then poured into water, no benzoic acid will be found in the liquid. (Liebig.) — 8. The aqueous solution is not decomposed by *chlorine gas*, but when it is boiled with a large excess of *chloride of lime* decomposition takes place. (Liebig.) — When chlorine gas is passed into an aqueous solution of hippuric acid, nitrogen is evolved and benzoglycolic acid produced. (Gössmann):

$$C^{18}NH^{9}O^{6} + 3KO + 3Cl = C^{18}H^{8}O^{8} + N + HO + 3KCl.$$

9. When hippuric acid is boiled with *peroxide of manganese* and very dilute sulphuric acid, a large quantity of carbonic acid is evolved, benzoic acid separates on cooling, and the liquid contains sulphate of ammonia. (Pelouze.) — 10. Hippuric acid boiled with *peroxide of lead* and water yields benzamide, carbonic acid and water (Fehling):

$$C^{18}NH^{9}O^{6} + 6O = C^{14}NH^{7}O^{2} + 4CO^{2} + 2HO.$$

When hippuric acid is heated with peroxide of lead, and excess of nitric or sulphuric acid, the products formed are carbonic acid and hipparaffin. (Schwarz, *Ann. Pharm.* 75, 195.) — When hippuric acid is boiled with water and peroxide of lead, and sulphuric acid is added from time to time in quantity only just sufficient to decompose the resulting hippurate of lead, the only product formed is benzamide. — During the action of peroxide of lead upon hippuric acid, a peculiar gas is produced, which irritates the eyes and lungs; and the water which distils over at the same time reddens litmus slightly, reduces nitrate of silver when mixed with

ammonia, but does not lose its peculiar odour on the addition of potash: it cannot therefore be formic acid. (Schwarz.) — 10. Hippuric acid gently heated with excess of lime, does not give off a trace of ammonia, but yields a liquid which smells of benzol, and when treated with hydrochloric acid, is converted into white crystalline scales; after rectification however it yields pure benzol [benzonitrile? *L.*] (Gerhardt.) — 11. By the action of a *ferment* in presence of an alkali, hippuric acid is resolved into benzoic acid and glycocol. (Buchner, *Ann. Pharm.* 78, 203.)

*Combinations.* Hippuric acid dissolves in 600 pts. of water at 0°, more readily in hot water. (Liebig.)

It decomposes the alkaline carbonates. The *Hippurates* are generally $C^{18}NH^8MO^6$, and most of them are soluble in water.

From their aqueous solutions, the hippuric acid is immediately precipitated by stronger acids in the form of a white crystalline powder, without previous turbidity as in the case of the benzoates. (Schwarz.)

*Hippurate of Ammonia.* — *a. Normal.* Crystallises with difficulty; the solution gives off ammonia when evaporated. (Liebig.)

*b. Acid.* — Crystallises by evaporation from a solution of hippuric acid in ammonia, even when the ammonia is in excess. Microscopic square prisms, acuminated with four faces resting on the edges. The crystals of the lower stratum are much better than those of the upper, which in fact consists of indistinct crystalline crusts. — The salt, after drying over oil of vitriol, gives off 4·115 p. c. (2 At.) of water at 100°. (Schwarz.)

| | *At* 100°. | | Schwarz. |
|---|---|---|---|
| 36 C | 216 | 54·95 | 54·61 |
| 3 N | 42 | 10·69 | |
| 23 H | 23 | 5·86 | 6·05 |
| 14 O | 112 | 28·50 | |
| $C^{18}NH^8(NH^4)O^6 + C^{18}NH^9O^6 + 2Aq$ | 393 | 100·00 | |

Between 180° and 200°, it gives off a large quantity of ammonia and leaves a red residue, which, when dissolved in water, yields rose-coloured crystals of hippuric acid. (Liebig, Schwarz.) — Dissolves very readily in water and alcohol, sparingly in ether. (Schwarz.)

*Hippurate of Potash.* — *a. Normal.* — Hippuric acid is dissolved in carbonate of potash; the excess of the alkali carefully neutralised with aqueous hippuric acid; and the resulting crystals purified by recrystallisation from alcohol, washing with ether, and finally by several crystallisations from hot water. If too much acid has been added, the acid hippurate of potash crystallises out first. If the crystals are immediately dried after being washed with ether, they deliquesce into a gummy mass. (Schwarz.)

| | *At* 100°. | | Schwarz. |
|---|---|---|---|
| KO | 47·2 | 21·73 | 21·74 |
| 18 C | 108·0 | 49·72 | 49·58 |
| N | 14·0 | 6·44 | |
| 8 H | 8·0 | 3·68 | 3·87 |
| 5 O | 40·0 | 18·43 | |
| $C^{18}NKH^8O^6$ | 217·2 | 100·00 | |

| | *Crystallised.* | | | Schwarz. |
|---|---|---|---|---|
| KO | 47·2 | 20·06 | | 19·91 |
| 18 C | 108·0 | 45·92 | | 45·78 |
| N | 14·0 | 5·95 | | |
| 10 H | 10·0 | 4·25 | | 4·30 |
| 7 O | 56·0 | 23·82 | | |
| $C^{18}NKH^{8}O^{6}$ + 2Aq | 235·2 | 100·00 | | |

The salt when charred gives off an agreeable odour, like that of *Satureja hortensis*, and quite different from that which is emitted by free hippuric acid. It dissolves readily in water, but is not precipitated therefrom by alcohol or ether; it dissolves in absolute alcohol or ether, sparingly when cold, more readily when warm, and crystallises therefrom on cooling. (Schwarz.)

*b. Acid.*—Obtained by dissolving an excess of hippuric acid in carbonate of potash.—Crystallises, even by slight concentration, in broad satiny laminæ, which under the microscope appear like square prisms with truncated terminal edges. Gives off 4·77 p. c. (2 At.) water at 100°. (Schwarz.)

| | *At* 100°. | | | Schwarz. |
|---|---|---|---|---|
| KO | 47·2 | 11·18 | | 11·28 |
| 36 C | 216·0 | 51·26 | | 52·01 |
| 2 N | 28·0 | 6·63 | | |
| 19 H | 19·0 | 4·50 | | 4·72 |
| 14 O | 112·0 | 26·43 | | |
| $C^{18}NH^{8}KO^{6}$ + $C^{18}NH^{9}O^{6}$ + 2Aq | 422·2 | 100·00 | | |

Probably nothing but hippuric acid mixed with the normal salt. Schwarz's analysis was made with too small a quantity. (Gerhardt, *N. J. Pharm.* 21, 314)

*Hippurate of Soda.*—Obtained by carefully neutralising hippuric acid with carbonate of soda, evaporating to dryness, and dissolving in alcohol. Crystalline mass having a slight yellowish colour. After drying over oil of vitriol, it does not give off any water at 100°. (Schwarz.)

| | | | | Schwarz. |
|---|---|---|---|---|
| 2 NaO | 62 | 15·07 | | 15·01 |
| 36 C | 216 | 52·55 | | 52·57 |
| 2 N | 28 | 6·81 | | |
| 17 H | 17 | 4·14 | | 4·29 |
| 11 O | 88 | 21·43 | | |
| $2(C^{18}NH^{8}NaO^{6})$ + Aq | 411 | 100·00 | | |

*Hippurate of Baryta.*—*a. Basic.*—When the aqueous solution of the acid is boiled with carbonate of baryta, and filtered, the alkaline liquid gelatinises on evaporation; yields as it cools, white porcelain-like crystals; and afterwards solidifies completely. The mass, after drying in vacuo, melts without loss when heated, and forms a transparent glass. (Liebig.)

*b. Normal.*—When the salt *a* is dissolved in water and acetic acid added till a slight acid reaction is produced, the normal salt crystallises in transparent laminæ. (Liebig.)—Hippuric acid is dissolved in excess of baryta-water, and the excess of baryta precipitated by carbonic acid; or carbonate of baryta is treated with excess of aqueous hippuric acid, the carbonate of baryta

being kept in excess. The solution, when evaporated, yields crystalline crusts consisting of microscopic square prisms. After drying over oil of vitriol, it gives off 3·74 p. c. (1 At.) water at 100°. (Schwarz.)

| | *At* 100°. | | | Schwarz. |
|---|---|---|---|---|
| BaO | 76·6 | .... | 31·06 | ..... 30·85 |
| 18 C | 108·0 | .... | 43·79 | ..... 43·99 |
| N | 14·0 | .... | 5·68 | |
| 8 H | 8·0 | .... | 3 24 | ..... 3·46 |
| 5 O | 40·0 | .... | 16·23 | |
| $C^{18}NH^{8}BaO^{6}$ | 246·6 | .... | 100·00 | |

| | *Crystallised.* | | | Schwarz. |
|---|---|---|---|---|
| BaO | 76·6 | .... | 29·97 | |
| 18 C | 108·0 | .... | 42·25 | ..... 41·79 |
| N | 14·0 | .... | 5·48 | |
| 9 H | 9·0 | .... | 3·52 | ..... 3·73 |
| 6 O | 48·0 | .... | 18·78 | |
| $C^{18}NH^{8}BaO^{6}$ + Aq | 255·6 | .... | 100·00 | |

*Hippuro-benzoate of Baryta.* — A mixture of benzoic and hippuric acids — whether in equivalent proportion or not — saturated with baryta-water, treated with carbonic acid, boiled, filtered, and evaporated, deposits at first, silvery laminæ of benzoic acid, then by further evaporation, waxy, rhombic tables of hippurate of baryta, and at last, the syrupy mother-liquor yields dull crystalline nodules of the double salt, which may be picked out from the admixed crystals of hippurate of baryta, and recrystallised from water. The salt gives off 7·49 p. c. (4 At.) water at 100°. (Schwarz, *Ann. Pharm.* 75, 192.)

| | *At* 100°. | | | Schwarz. |
|---|---|---|---|---|
| 2 BaO | 153·2 | .... | 34·42 | ..... 34·24 |
| 32 C | 192·0 | .... | 43·13 | ..... 43·42 |
| N | 14·0 | .... | 3·14 | ..... 3·61 |
| 14 H | 14·0 | .... | 3·14 | ..... 3·59 |
| 9 O | 72·0 | .... | 16·17 | ..... 15·14 |
| $C^{14}H^{5}BaO^{4}$ + $C^{18}H^{8}BaO^{6}$ + Aq | 445·2 | .... | 100·00 | ..... 100·00 |

*Hippurate of Strontia.* — Carbonate of strontia is dissolved in aqueous hippuric acid, and the crystals several times recrystallised from cold alcohol. — From its hot solution in water or alcohol, the salt crystallises in broad laminæ, which fill the entire liquid, and under the microscope appear as square prisms with perpendicular terminal faces. — It dissolves somewhat sparingly in cold water and alcohol, readily in hot. Gives off 3·74 p. c. (5 At.) water at 100°. (Schwarz.)

| | *At* 100°. | | | Schwarz. |
|---|---|---|---|---|
| SrO | 51·8 | .... | 23·35 | ..... 23·42 |
| 18 C | 108·0 | .... | 48·69 | ..... 48·83 |
| N | 14·0 | .... | 6·31 | |
| 8 H | 8·0 | .... | 3·61 | ..... 4·01 |
| 5 O | 40·0 | .... | 18·04 | |
| $C^{18}NH^{8}SrO^{6}$ | 221·8 | .... | 100·00 | |

| | *Crystallised.* | | | Schwarz. |
|---|---|---|---|---|
| SrO | 51·8 | .... | 19·41 | 19·40 |
| $C^{18}NH^{8}O^{5}$ | 170·0 | .... | 63·72 | |
| 5 HO | 45·0 | .... | 16·87 | 16·23 |
| $C^{18}NH^{8}SrO^{6} + 5Aq$ | 266·8 | .... | 100·00 | |

*Hippurate of Lime.* — Hippuric acid is dissolved in milk of lime, the solution filtered, carbonic gas was passed through the filtrate, the liquid again filtered, and the clear solution left to crystallise. (Schwarz.) The aqueous solution of the acid heated with carbonate of lime, yields rhombic tables on cooling, and shining laminæ by evaporation. (Liebig.) Oblique rhombic tables. (Schwarz.) Four-sided prisms belonging to the right prismatic system. Faces *u*, *u'*, *a*, *a'*, *ii* and *z*; $u : u' = 83° 44'$; $a : a' = 114° 18'$; $a : a' = 134° 18'$. Ratio of the axes = 1 : 1·9244 : 0·3697. (Schabus.) Sp. gr. 1·318. (Schabus, *Wien. Akad.* 1850, 2,214.) Gives off 11·97 p. c. (3 At.) water at 100°.

| | *At* 100°. | | | Schwarz. |
|---|---|---|---|---|
| CaO | 28 | .... | 14·14 | 14·31 |
| 18 C | 108 | .... | 54·54 | 54·40 |
| N | 14 | .... | 7·07 | |
| 8 H | 8 | .... | 4·04 | 4·01 |
| 5 O | 40 | .... | 20·21 | |
| $C^{18}H^{8}CaO^{6}$ | 198 | .... | 100·00 | |

| | *Crystallised.* | | | Liebig. | Schwarz. |
|---|---|---|---|---|---|
| CaO | 28 | .... | 12·44 | 12·53 | |
| $C^{18}NH^{8}O^{5}$ | 170 | .... | 65·57 | | |
| 3 HO | 27 | .... | 11·99 | | 12·00 |
| $C^{18}H^{8}CaO^{6} + 3Aq$ | 225 | .... | 100·00 | | |

*Hippurate of Magnesia.* — Obtained by dissolving carbonate of magnesia in the aqueous acid. Crystallises from a tolerably concentrated solution in crystalline nodules, which must be washed with the smallest possible quantity of water. After drying over oil of vitriol, it gives off 15·35 p. c. (4 At.) water at 100°.

| | *At* 100°. | | | Schwarz. |
|---|---|---|---|---|
| MgO | 20 | .... | 10·07 | 10·04 |
| 18 C | 108 | .... | 54·27 | 53·74 |
| N | 14 | .... | 7·03 | |
| 9 H | 9 | .... | 4·52 | 5·05 |
| 6 O | 48 | .... | 24·11 | |
| $C^{18}NH^{8}MgO^{6} + Aq$ | 199 | .... | 100·00 | |

The salt dissolves in 18 pts. of cold and 6 pts. of boiling water. (Liebig.)

*Hippurate of Zinc.* — Zinc dissolves with evolution of hydrogen in aqueous hippuric acid at the boiling heat, and the liquid after boiling for some time, solidifies on cooling into a white crystalline magma. — The same salt separates in the crystalline form on mixing concentrated solu-

tions of a salt of hippuric acid, and sulphate or chloride of zinc.—Crystallises from the aqueous solution on cooling, in laminæ united in stellate groups. The crystals give off (5 At.) water at 100°; 1 pt. of the anhydrous salt dissolves in 53·2 pts. of water at 17·5°; in about 4 pts. at 100°; in 60·5 pts. of alcohol (sp. gr. 0·82), at 17·5°; in ether it is nearly insoluble. (J. Löwe, *J. pr. Chem.* 65, 369.)

*Hippurate of Lead.* — *a. Basic.* — When oxide of lead is boiled with hippuric acid and water, a portion dissolves, while the rest forms a viscid mass which soon turns black even under water. When the solution is evaporated, a crystalline film forms on the surface, and at a greater degree of concentration the whole solidifies in a white mass. (Liebig.)

*b. Normal.* — The hot solution of a hippurate mixed with neutral acetate of lead yields on cooling pearly laminæ, which effloresce in hot air. (Liebig.) Cold hippurate of potash forms with neutral acetate of lead a white curdy precipitate which dissolves sparingly in cold water. The solution diluted and filtered at the boiling heat through a hot funnel, deposits tufts of delicate silky needles, which often, especially in concentrated solutions, suddenly take up 1 At. water, and change completely into broad shining laminæ easily recognised as four-sided tables. The solution of the salt yields either the needle-shaped or the laminar crystals according to its degree of dilution and the time that it is left to stand. Both kinds of crystals give off their water of crystallisation at 100°. (Schwarz.)

| | *At* 100°. | | Schwarz. |
|---|---|---|---|
| PbO | 111·8 | 39·67 | 39·35 |
| 18 C | 108·0 | 38·33 | 38·50 |
| N | 14·0 | 4·97 | |
| 8 H | 8·0 | 2·84 | 3·02 |
| 5 O | 40·0 | 14·19 | |
| $C^{18}NH^{8}PbO^{6}$ | 281·8 | 100·00 | |

| | *Needles.* | | Schwarz. |
|---|---|---|---|
| PbO | 111·8 | 37·28 | 36·92 |
| $C^{18}NH^{8}O^{5}$ | 170·0 | 56·72 | |
| 2 HO | 18·0 | 6·00 | |
| $C^{18}NH^{8}PbO^{6}$ + 2Aq | 299·8 | 100·00 | |

| | *Laminæ.* | | Liebig. | Schwarz. |
|---|---|---|---|---|
| PbO | 111·8 | 36·20 | 35·94 | 36·08 |
| $C^{18}NH^{8}O^{5}$ | 170·0 | 55·05 | | |
| 3 HO | 27·0 | 8·75 | | |
| $C^{18}NH^{8}PbO^{6}$ + 3Aq | 308·8 | 100·00 | | |

*Ferric Hippurate.* — Soluble hippurates form a rust-brown precipitate with ferric salts. (Liebig.) — Neutral sesquichloride of iron forms with cold hippurate of potash, a light cream-coloured bulky precipitate, which, when immersed in hot water or dried at 30°, gives up water, and deliquesces to a brown mass having the consistence of temperature. — The salt is insoluble in water, dissolves readily in alcohol especially when

hot, and separates as the solution cools, partly in the amorphous state, partly in tufts of red oblique rhombic prisms.

*Hippurate of Cobalt.* — Carbonate of cobalt forms with aqueous hippuric acid a red solution, from which the hippurate of cobalt is precipitated by alcohol; it may then be washed with alcohol and recrystallised from water. Rose-coloured nodules consisting of concentrically grouped microscopic four-sided prisms which, after drying over oil of vitriol give off 17·53 per cent. (5 At.) water at 100°, and assume a violet colour. (Schwarz.)

| | *At* 100°. | | | Schwarz. |
|---|---|---|---|---|
| CoO | 37·6 | | 18·11 | 17·90 |
| 18 C | 108·0 | | 52 02 | 51·97 |
| N | 14·0 | | 6·74 | |
| 8 H | 8·0 | | 3·85 | 4·06 |
| 5 O | 40·0 | | 19·28 | |
| $C^{18}NH^{8}CoO^{6}$ | 207·6 | | 100·00 | |

*Hippurate of Nickel.* — Obtained by treating carbonate of nickel in excess with aqueous hippuric acid. The solution, after evaporation over oil of vitriol, yields indistinct crystalline crusts of an apple-green colour. The salt dissolves very sparingly in cold water, better in hot water or alcohol, but is insoluble in ether. (Schwarz.)

| | *At* 100°. | | | Schwarz. |
|---|---|---|---|---|
| NiO | 37·6 | | 18·11 | 18·02 |
| 18 C | 108·0 | | 52·02 | 51·62 |
| N | 14·0 | | 6·74 | |
| 8 H | 8·0 | | 3·85 | 4·13 |
| 5 O | 40·0 | | 19·28 | |
| $C^{18}NH^{8}NiO^{6}$ | 207·6 | | 100·00 | |

| | *Crystallised.* | | | Schwarz. |
|---|---|---|---|---|
| NiO | 37·6 | | 14·86 | |
| 18 C | 108·0 | | 42·76 | 42·75 |
| N | 14·0 | | 5·55 | |
| 13 H | 13·0 | | 5·15 | 5·85 |
| 10 O | 80·0 | | 31·68 | |
| $C^{18}NH^{8}NiO^{6}$ + 5Aq | 252·6 | | 100·00 | |

*Hippurate of Copper.* — Separates, on evaporating a solution of sulphate of copper mixed with a soluble hippurate, in green crystals which may be recrystallised from hot alcohol. Microscopic oblique rhombic prisms sparingly soluble in cold water, readily in hot alcohol. After being dried over oil of vitriol, the salt gives off 13·33 per cent. (3 At.) of water at 100°.

| | *At* 100°. | | | Schwarz. |
|---|---|---|---|---|
| CuO | 39·8 | | 18·97 | 18·77 |
| 18 C | 108·0 | | 51·48 | 51·39 |
| N | 14·0 | | 6·68 | |
| 8 H | 8·0 | | 3·81 | 4·04 |
| 5 O | 40·0 | | 19·06 | |
| $C^{18}NH^{8}CuO^{6}$ | 209·8 | | 100·00 | |

| | *Crystallised.* | | | Schwarz. |
|---|---|---|---|---|
| CuO | 39·8 | .... | 16·81 | |
| 18 C | 108·0 | .... | 45·61 | ..... 45·52 |
| N | 14·0 | .... | 5·91 | |
| 11 H | 11·0 | .... | 4·64 | ..... 4·91 |
| 8 O | 64·0 | .... | 27·03 | |
| $C^{18}NH^{8}CuO^{6}$ + 3Aq | 236·8 | .... | 100·00 | |

*Mercurous Hippurate.* — Soluble hippurates form a white curdy precipitate with mercurous nitrate.

*Hippurate of Silver.* — Hippurate of potash forms with nitrate of silver a white curdy precipitate; and when this precipitate is dissolved in boiling water and the solution filtered hot, silky needles separate on cooling. — The salt, after drying over oil of vitriol, gives off 3·42 p. c. (1 At.) of water at 100°. (Schwarz.)

| | *At* 100°. | | | Dumas & Peligot. | | Schwarz. |
|---|---|---|---|---|---|---|
| 18 C | 108 | .... | 37·76 | | | 37·57 |
| N | 14 | .... | 4·89 | | | |
| Ag | 108 | .... | 37·76 | ..... 37·33 | .... | 37·21 |
| 8 H | 8 | .... | 2·80 | | | 2·86 |
| 6 O | 48 | .... | 16·79 | | | |
| $C^{18}NH^{8}AgO^{6}$ | 286 | .... | 100·00 | | | |

| | *Crystallised.* | | | Liebig. | | Schwarz. |
|---|---|---|---|---|---|---|
| 18 C | 108 | .... | 36·61 | | | 36·44 |
| N | 14 | .... | 4·75 | | | |
| Ag | 108 | .... | 36·61 | ..... 36·40 | .... | 36·32 |
| 9 H | 9 | .... | 3·05 | | | 3·10 |
| 7 O | 56 | .... | 18·98 | | | |
| $C^{18}NH^{8}AgO^{6}$ + Aq | 295 | .... | 100·00 | | | |

Hippuric acid dissolves readily in *alcohol*, sparingly in *ether*.

## Hippurate of Ethyl.

$C^{22}NH^{13}O^{6} = C^{4}H^{5}O,C^{18}NH^{8}O^{5}$.

STENHOUSE. *Ann. Pharm.* 31, 148.
LIEBIG. *Ann. Pharm.* 65, 351.

*Formation and Preparation.* — 1. When an alcoholic solution of hippuric acid saturated while hot is left to stand for some months in a warm place, hippuric acid separates at first in cauliflower-like masses (p. 72), and ultimately, crystals are formed which exhibit the characters of hippuric ether. (Liebig.) — 2. A solution of hippuric acid in alcohol of sp. gr. 0·815 is distilled for several hours, while hydrochloric acid gas is continually passed through it, the alcohol which distils over being repeatedly poured back. As soon as the liquid has become thick and

oily, the hippuric ether may be precipitated by water, in the form of a thick oil, which solidifies in the crystalline form after being freed from the alcohol and the acid. (Stenhouse.)

*Properties.* Crystallises from a somewhat dilute alcoholic solution in white silky needles unctuous to the touch. Inodorous. Tastes like turpentine. Sp. gr. 1·043. Melts at 44°, and solidifies in the crystalline form at 32°. (Stenhouse.)

| | | | | | Stenhouse. |
|---|---|---|---|---|---|
| 22 C | 132 | 63·77 | 63·72 | | 62·89 |
| N | 14 | 6·76 | | | 5·56 |
| 13 H | 13 | 6·28 | | | 6·42 |
| 6 O | 48 | 23·19 | | | 25·13 |
| $C^{22}NH^{13}O^{6}$ | 207 | 100·00 | | | 100·00 |

*Decompositions.* 1. The ether is partially decomposed by *distillation*, the odour of bitter almonds then becoming perceptible. When heated in contact with the air, it gives off benzoic acid and afterwards takes fire. — 2. When heated with *nitric acid*, it gives off nitric oxide gas, and yields hippuric acid at a gentle heat, benzoic acid on boiling. — 3. *Hydrochloric acid* decomposes hippuric ether into hippuric acid and alcohol. — 4. When the ether is heated with *oil of vitriol*, it blackens and yields benzoic acid.—5. Dry *chlorine gas* is absorbed by fused hippuric ether, with evolution of hydrochloric acid. After the excess of chlorine has been driven off, a white substance is obtained, which smells like chloride of benzoyl, does not yield benzoic acid when treated with water, dissolves sparingly in water, readily in alcohol and ether, and separates from the solution in tufted crystals, heavier than water and perfectly neutral. When heated with potash-ley, they yield chloride of potassium, and the liquid when acidulated, deposits crystals which do not resemble either hippuric or benzoic acid. — 6. Hippuric ether heated with *potash-ley*, is resolved into alcohol and hippuric acid. *Solution of ammonia* acts in the same manner; dry ammoniacal gas does not act upon hippuric ether. (Stenhouse.)

*Appendix to Hippuric Acid.*

## Hipparaffin.

$C^{16}NH^{7}O^{2}$(= $C^{14}CyH^{6}$ + 2HO ? Gm.).

H. Schwarz. *Ann. Pharm.* 75, 201.

From ἵππος, and *parum affinis*.

*Formation and Preparation.* By heating hippuric acid, water, and peroxide of lead with a quantity of sulphuric, phosphoric, or nitric acid, larger than is required to neutralise the resulting protoxide of lead. — Hippuric acid is gently heated with water and a large excess of peroxide

of lead and sulphuric acid; the pasty mass thrown upon a filter while still hot; and the acid completely washed out with water. — (The liquid deposits a small additional quantity of hipparaffin on cooling, and the solution filtered therefrom yields a still larger quantity, after being saturated with ammonia and evaporated; a small quantity of benzamide is also formed, and a portion of the hippuric acid remains unaltered, if the heating has not been long enough continued.) — The residue on the filter is dried, pulverised, boiled with tolerably strong alcohol, filtered hot, and the residue washed with boiling alcohol. The alcoholic solution, cooled and evaporated, yields needles of hipparaffin down to the last drop. These crystals are dried over oil of vitriol—if heated, they might deliquesce in consequence of alcohol adhering to them—then boiled and washed with water containing a little ammonia.

*Properties.* Crystallises from hot alcohol in extremely fine soft needles having a silky lustre and arranged in thickly interlaced bundles. Inodorous and tasteless. Melts at 200°, solidifying in the crystalline form as it cools; at a stronger heat, part of it distils without alteration, the residue turning black.

| | | | Schwarz. |
|---|---|---|---|
| 16 C | 96 | 71·64 | 71·44 |
| N | 14 | 10·45 | 10·53 |
| 8 H | 8 | 5·97 | 6·09 |
| 2 O | 16 | 11·94 | 11·94 |
| $C^{16}NH^{8}O^{2}$ | 134 | 100·00 | 100·00 |

*Decompositions.* 1. Burns with a bright sooty flame, leaving a small quantity of easily combustible charcoal. — 2. In nitric acid, even when concentrated, it dissolves without decomposition at ordinary temperatures, and is separated again by water without alteration; the solution, when heated, gives off a small quantity of gas, and after a while no longer yields hipparaffin on the addition of water. Hipparaffin dissolves in cold red fuming nitric acid, and melts into an oil; but if the liquid has not been heated to the boiling point, it is separated without alteration on mixing the liquid with water. — 3. Hipparaffin is not decomposed by solution of iodine, by chlorate of potash and hydrochloric acid, or by aqueous chromic acid. — 4. When fused with caustic potash it is but partially decomposed, with evolution of ammonia; the undecomposed portion separates again on addition of water. — When hipparaffin is ignited with potash lime, benzol is produced, and the whole of the nitrogen goes off in the form of ammonia.

Hipparaffin dissolves sparingly in hot *water*, but is quite insoluble in cold water, which does not even wet it; the solubility is not increased by addition of sulphuric acid, hydrochloric acid, ammonia or potash. Hipparaffin dissolves readily and without colour in *oil of vitriol*, and is precipitated by water without much alteration. It dissolves readily in boiling *alcohol*, and very readily in *ether*.

## ¶. Benzoate of Allyl.

$C^{20}H^{10}O^{4} = C^{6}H^{5}O,C^{14}H^{5}O^{3}$.

ZININ. *Petersb. Akad. Bull.* 13, 360; *J. pr. Chem.* 65, 269; *Ann. Pharm.* 96, 362.
CAHOURS & HOFMANN. *Phil. Trans.* 1857, ii, 9; *Ann. Pharm.* 102, 297.
BERTHELOT & DE LUCA. *N. Ann. Chim. Phys.* 48, 286.

*Benzoate of Propylenyl, Benzoate of Acryl.*

*Formation and Preparation.* By the action of iodide of allyl on benzoate of silver (Zinin, Cahours & Hofmann, Bethelot & De Luca), or of chloride of benzoyl on allylic alcohol. (Cahours & Hofmann.)

$$[C^{14}H^{5}O^{2},Cl + \left.\begin{matrix}C^{6}H^{5}\\H\end{matrix}\right\}O^{2} = \left.\begin{matrix}C^{14}H^{5}O^{2}\\C^{6}H^{5}\end{matrix}\right\}O^{2} + HCl].$$

Zinin rectifies the product obtained by the first method over benzoate of silver, washes the distillate with carbonate of soda, dries it over chloride of calcium, then rectifies it over oxide of lead, and lastly *per se*.

*Properties.* Yellow, oily, neutral liquid, heavier than water, and having an odour like that of benzoate of ethyl. Boils at 242° (Zinin), at 228° (Cahours & Hofmann), at 230° (Berthelot & De Luca).

| | | | Zinin. | Cahours & Hofmann. |
|---|---|---|---|---|
| 20 C | 120 | 74·07 | 74·29 | 73·10 |
| 10 H | 10 | 6·17 | 6·44 | 6·24 |
| 4 O | 32 | 19·76 | 19·37 | 20·66 |
| $C^{20}H^{10}O^{4}$ | 162 | 100·00 | 100·00 | 100·00 |

By boiling with potash-ley, it is converted into benzoate of potash and allylic alcohol. (Cahours & Hofmann; Berthelot & De Luca.)

It is insoluble in water, but dissolves in *wood-spirit, alcohol,* and *ether* ¶.

## Benzoate of Amyl.

$C^{26}H^{16}O^{4} = C^{10}H^{11}O,C^{14}H^{5}O^{3}$.

RIECKHER. *Jahrb. pr. Pharm.* 14, 15; abstr. *Ann. Pharm.* 64, 336; *N. J. Pharm.* 14, 300.

Obtained by distilling a mixture of 1 pt. fusel-oil and 2 pts. oil of vitriol with excess of an alkaline benzoate (Rieckher);—or by saturating a solution of benzoic acid in amylic alcohol with hydrochloric acid gas, washing the product with aqueous carbonate of soda, then (since it sepa-

rates but slowly from water on account of its nearly equal density), with solution of chloride of calcium, and rectifying. (H. Kopp, *Ann. Pharm.* 94, 311.)

Liquid having a faint yellowish colour, and a peculiar, not unpleasant odour. (Rieckher.) Sp. gr 0·9925 at 14·4° or 1·0039 at 0°. (Kopp.) Boils between 252° and 254° (Rieckher); at 260·7° with the barometer at 745·6 mm. (Kopp.)

| | | | Rieckher. |
|---|---|---|---|
| 24 C | 144 | 75·21 | 75·43 |
| 16 H | 16 | 8·20 | 8·51 |
| 4 O | 32 | 16·59 | 16·06 |
| $C^{24}H^{16}O^4$ | 192 | 100·00 | 100·00 |

It is easily decomposed by alcoholic potash.

## Benzone.

$$C^{26}H^{16}O^2 = C^{14}H^6O^2,C^{12}H^4.$$

MITSCHERLICH. *Pogg.* 29, 231.
PELIGOT. *Ann. Chim. Phys.* 56, 59; also *Ann. Pharm.* 12, 39; *Pogg.* 36, 69.
LIEBIG. *Ann. Pharm.* 12, 50.
CHANCEL. *Compt. rend.* 28, 83; *Compt. chim.* 1849, 87.—Further, *Compt. chim.* 1851, 85; also *J. pr. Chem.* 53, 252; abstr. *Ann. Pharm.* 80, 285.

*Carbobenzid, Benzophenone, Oxide d'Essène.*

*Formation and Preparation.* 1. Dry benzoate of lime mixed with $\frac{1}{10}$ of quick lime is distilled from an iron mercury-bottle. When the crude distillate is several times redistilled, a large quantity of benzol passes over at first, the boiling point then rising rapidly; and above 315° or 325°, nearly pure benzone distils over, solidifying into a straw-coloured mass; it may be obtained pure by crystallisation from a mixture of ether and alcohol. The quantity of benzone obtained is equal to $\frac{1}{4}$ the weight of the lime-salt. (Chancel.) — 2. The crude distillate is dissolved in oil of vitriol and after a few days, sufficient water is added to render the liquid turbid; there is then formed on the surface a very abundant crystalline layer, which is to be taken off, washed with water, and crystallised from a mixture of ether and alcohol. (Chancel.) — 3. Strong nitric acid acts very violently on the crude distillate; if the action has not been carried too far, a brown viscid mass is obtained insoluble in water but easily soluble in alcohol and ether. If the solution in ether-alcohol is mixed with hydrosulphate of ammonia, the benzone separates in beautiful yellow crystals. (Chancel.)— Peligot heated crystallised benzoate of lime to about 300° and distilled the liquid which passed over with water. A large quantity of benzol then passed over and the residue distilled over the open fire, yielded, first water, and then an oil which boiled at 250°, from which naphthalin (?) separated at—20°. The slightly empyreumatic oil, floating on water and boiling at 250°, which was decanted from this substance, contained 87·35 C and 5·65 H, and was called benzone by Peligot; but according to Chancel, it is a mixture of the true benzone (Chancel's benzophenone) with hydrocarbons, bitter almond oil, &c.

*Properties.* Thick, transparent, pale yellow rhombic prisms, of 99°, with hexagonal summits. Melts at 46° to a thick oil, which solidifies only on agitation. Has a pleasant slightly ethereal odour somewhat like that of benzoate of ethyl. Boils at 315°, and volatilises undecomposed. (Chancel.)

| | | | | Chancel. |
|---|---|---|---|---|
| 26 C | 156 | | 85·71 | 85·70 |
| 10 H | 10 | | 5·50 | 5·57 |
| 2 O | 16 | | 8·79 | 8·73 |
| $C^{26}H^{10}O^{2}$ | 182 | | 100·00 | 100·00 |

The ketone of the benzylene-series. — According to Mitscherlich, it is benzol conjugated with carbonic oxide: $C^{26}H^{10}O^{2} = 2(C^{12}H^{6},CO)$.

*Decompositions.* 1. The vapour is easily set on fire and burns with a bright flame.

2. Benzone boiled with fuming nitric acid forms a thick oil very soluble in ether, which retains its fluidity for a long time in the cold, but separates almost instantly from its ethereal solution in the form of a pale yellowish powder; this oil is *binitrobenzone* (*benzophénone binitré*) $= C^{26}X^{2}H^{8}O^{2}$.

| | *Binitrobenzone.* | | | Chancel. |
|---|---|---|---|---|
| 26 C | 156 | | 57·35 | 57·18 |
| 2 N | 28 | | 10·30 | 10·55 |
| 8 H | 8 | | 2 94 | 3·03 |
| 10 O | 80 | | 29·41 | 29·24 |
| $C^{26}(NO^{4})^{2}H^{8}O^{2}$ | 272 | | 100·00 | 100·00 |

Binitrobenzone treated with hydrosulphate of ammonia yields flavine. (Chancel.)

3. With *potash-lime* at about 260°, benzone yields benzoic acid and pure benzol, without evolution of hydrogen. (Chancel):

$$C^{26}H^{10}O^{2} + KO,HO = C^{14}H^{5}KO^{4} + C^{12}H^{6}.$$

*Combinations.* Benzone is not soluble in water. It dissolves abundantly in *oil of vitriol* and in *nitric acid*, and is separated from the solution by water in its original state. It dissolves with tolerable facility in *alcohol*, and very readily in *ether*.

## Benzoate of Phenyl.

$$C^{26}H^{10}O^{4} = C^{12}H^{5}O,C^{14}H^{5}O^{3}.$$

ETTLING. (1845.) *Ann. Pharm.* 53, 87; abstr. *J. pr. Chem.* 26, 262.— *Phil. Mag. J.* [3] 27, 3.
STENHOUSE. *Ann. Pharm.* 53, 91; 55, 10.
LAURENT & GERHARDT. *Compt. chim.* 1849, 429. *Ann. Pharm.* 75, 75.
GERHARDT. *Ann. Pharm.* 87, 161.
LIST & LIMPRICHT. *Ann. Pharm.* 90, 190.

*Benzoesaure Carbolsäure, Benzoeoxyd, Benzoyloxyd, Phänidin, Benzophänid, Benzoyl, benzoesaures Phenyloxyd.*—Ettling and Stenhouse regarded the substance formed by the dry distillation of benzoate of copper as an oxide $C^{14}H^{5}O^{2}$, standing below benzoic acid; Gerhardt prepared the same substance from anhydrous benzosalicylic acid, and regarded it as the radical benzoyl (p. 23); List & Limpricht have shown that the substance obtained by either of these processes is identical with Laurent & Gerhardt's benzophenide.

*Formation.* 1. By heating chloride of benzoyl with carbolic acid [or by the action of chloride of benzoyl on carbolate of potassium. (Williamson, *Proc. Roy. Soc.* 7, 18.)] — 2. By the dry distillation of benzoate of copper. — 3. By heating anhydrous benzo-salicylic acid.

*Preparation.* 1. Carbolic acid is heated with chloride of benzoyl, the addition of the latter being continued as long as hydrochloric acid continues to escape, and the cooled crystalline mass is dissolved in a mixture of ether and alcohol; on leaving the solution to evaporate, the compound crystallises in needles. A small quantity of benzoic ether separates at the same time, being formed by the action of the excess of chloride of benzoyl on the alcohol. (Laurent & Gerhardt.) — 2. Dry benzoate of copper is distilled at a temperature not exceeding 220°; the sublimate which forms in the neck of the retort, freed from admixed benzoic acid by means of dilute potash; and the residue repeatedly crystallised from alcohol. (Ettling.) Stenhouse treats the crystalline mass with carbonate of soda after pressing it between paper, and crystallises the washed residue several times from alcohol or ether. — Dry benzoate of copper is distilled over the open fire as long as vapours continue to escape; the buttery distillate covered with water, then supersaturated with carbonate of soda, and distilled as long as oily drops of benzol continue to pass over with the watery vapours. The residue is separated from the liquid containing carbonate of soda, washed with water and dissolved in hot alcohol. The crystals which separate on cooling, and are contaminated with an oily body, are heated with a small quantity of alcohol, which chiefly dissolves the oil, and repeatedly crystallised from hot alcohol. (List & Limpricht.) — 3. Anhydrous benzo-salicylic acid is heated, and the product boiled with potash ley; the oil which floats on the liquid solidifies in the crystalline form on cooling, and yields needles when crystallised from alcohol. (Gerhardt.)

*Properties.* Colourless, transparent, hard, shining, rhombic prisms often half an inch long. Fig. 81; $\acute{u} : u = 100° 48' 24''$; $u : \acute{i} = 81° 22' 19''$. Ratio of the axes = 1 : 1·2089 : 0·1962. (Dauber.) Has a faint agreeable odour of geraniums and lemons, especially when heated. Melts at 59° (Ettling); at 70° (Stenhouse); at 66° (Gerhardt; List and Limpricht). Solidifies at 42° in a radiated crystalline mass. — At a higher temperature (above 100°, according to List & Limpricht), it appears to volatilise without decomposition.

| | | | Ettling. | Will. | Stenhouse. | Laurent & Gerhardt. | Gerhardt. | List & Limpricht. |
|---|---|---|---|---|---|---|---|---|
| 26 C | 156 | 78·79 | 78·65 | 78·76 | 79·81 | 78·4 | 79·53 | 78·21 |
| 10 H | 10 | 5·05 | 5·05 | 5·06 | 5·11 | 5·0 | 5·05 | 5·04 |
| 4 O | 32 | 16·16 | 16·30 | 16·18 | 15·08 | 16·6 | 15·42 | 16·75 |
| $C^{26}H^{10}O^{4}$ | 198 | 100·00 | 100·00 | 100·00 | 100·00 | 100·0 | 100·00 | 100·00 |

*Decompositions.* 1. The compound burns in the air with a red, very smoky flame. — 2. Exposed to the action of *chlorine gas* for a day at a warm temperature, it is converted into a soft yellow mass consisting of a liquid and a solid chlorine-compound. (Stenhouse.) — 3. With liquid *bromine* it gives off hydrobromic acid gas, and is converted into benzoate of bromophenyl. (Laurent & Gerhardt, List & Limpricht.) — 4. Boiling nitric acid converts it into a yellow fused mass, with evolution of brown-red vapours (Laurent & Gerhardt); cold *nitro-sulphuric acid* converts it into nitrobenzoate of binitrophenyl. (List & Limpricht.) — 5. *Oil of vitriol* dissolves it, with slight evolution of heat; and on adding water to the solution, benzoic acid is precipitated and sulphocarbolic acid remains in solution. (Laurent & Gerhardt.) — 6. It is not altered by pentachloride of phosphorus. (List & Limpricht.) — 7. It is not decomposed by boiling with aqueous potash, and remains unaltered when heated with potash-ley to 120° in a sealed tube; if the heat be kept for some time at 150°, benzoate and carbonate of potash are produced. (List & Limpricht.) — The compound boiled with aqueous potash takes up oxygen and is converted into benzoic acid. (Stenhouse.) When fused with caustic potash, it forms carbolate and benzoate of potash (Laurent & Gerhardt, Gerhardt); (and gives off hydrogen. Stenhouse. [? L.]). Also when treated with alcoholic potash (Stenhouse), even in the cold. (List & Limpricht.) — 8. Heated in ammoniacal gas or boiled with an ammoniacal solution of ammonia, it yields carbolic acid and benzamide. (List & Limpricht.)

It is insoluble in water, but dissolves with tolerable facility in cold *alcohol* and *ether*, readily in the same liquids at higher temperatures.

## Benzoate of Bromophenyl.

$C^{26}H^{9}BrO^{4} = C^{12}H^{4}BrO,C^{14}H^{5}O^{3}$; and $C^{26}H^{8}Br^{2}O^{4} = C^{12}H^{3}Br^{2}O,C^{14}H^{5}O^{3}$.

List & Limpricht. *Ann. Pharm.* 90, 196.

*Benzoesaure Bromcarbolsaure, Benzoesaures Bromphenyloxyd.*

*Formation and Preparation.* Bromine is poured upon dry benzoate of phenyl in a retort, till no more hydrobromic acid gas is evolved, even on heating the liquid; the excess of bromine is then distilled off, and the mass which solidifies on cooling is washed with water and repeatedly crystallised from hot alcohol.

*Properties.* Large colourless needles arranged in arborescent groups; they melt below 100° and appear to sublime without decomposition

| *Calculation* 1. | | | | *Calculation* 2. | | | |
|---|---|---|---|---|---|---|---|
| 26 C | 156 | | 56·31 | 26 C | 156 | | 43·82 |
| 9 H | 9 | | 3·25 | 8 H | 8 | | 2·25 |
| Br | 80 | | 28·88 | 2 Br | 160 | | 44·94 |
| 4 O | 32 | | 11·56 | 4 O | 32 | | 8·99 |
| $C^{26}H^{9}BrO^{4}$ | 277 | | 100·00 | $C^{26}H^{8}Br^{2}O^{4}$ | 356 | | 100·00 |

*Calculation 3.*

| | | |
|---|---|---|
| 26 C | 156 | 35·86 |
| 7 H | 7 | 1·61 |
| 3 Br | 240 | 55·17 |
| 4 O | 32 | 7·36 |
| $C^{26}H^7Br^3O^4$ | 435 | 100·00 |

Analyses by List and Limpricht.

| | a. | b. | c. | d. |
|---|---|---|---|---|
| C | 55·59 | 54·79 | | 50·11 |
| H | 3·88 | 3·19 | | 2·93 |
| Br | | | 32 48 | 34·65 |
| O | | | | 12·31 |
| | | | | 100·00 |

| | e. | f. | g. | h. | i. |
|---|---|---|---|---|---|
| C | 46·55 | 43·15 | | | 42·74 |
| H | 2·46 | 2·59 | | | 2·04 |
| Br | | | 37·69 | 42·82 | 45·42 |
| O | | | | | 9·80 |
| | | | | | 100·00 |

The analyses show that the substance is a mixture of two, or probably, as indicated by analysis *i*, of three substitution-products, which cannot be separated from one another by crystallisation. No unaltered benzoate of phenyl could be present, because an excess of bromine was used in the preparation, and benzoate of phenyl dissolves pretty easily in cold alcohol.

The mother-liquor which remains after the first recrystallisation retains in solution an oily substance which separates when the liquid is very much concentrated; its solution in ether yields by evaporation small colourless crystals, perhaps consisting of the compound $C^{26}H^7Br^3O^4$.

*Decompositions.* 1. Cold *nitrosulphuric acid* converts the compound into nitrobenzoate of bromophenyl. — 2. It dissolves in *oil of vitriol,* forming a greenish solution from which water throws down benzoic acid; and the aqueous solution saturated with carbonate of baryta yields a soluble baryta-salt. — 3. Benzoate of bromophenyl dissolves readily in cold alcoholic potash; the solution does not become turbid on addition of water, but when treated with sulphuric acid, it deposits benzoic and bromocarbolic acids.

This compound is insoluble in water, very sparingly soluble in cold *alcohol* and *ether,* but dissolves readily in those liquids at higher temperatures.

## Benzoate of Chlorophenyl.

$C^{26}H^8ClO^4 = C^{12}H^4ClO,C^{14}H^5O^3$.

STENHOUSE. *Ann. Pharm.* 53, 95.
LIST & LIMPRICHT. *Ann. Pharm.* 90, 199.

*Benzoesaure Chlorcarbolsäure, benzoesaures Phenyloxyd.*

When chlorine gas is passed for several days over benzoate of phenyl, a dark yellow mixture is produced, consisting of an oily and a solid body,

which has a very disagreeable pungent odour, and strongly excites tears. This product is pressed between bibulous paper at a gentle heat, and the solid residue repeatedly recrystallised from ether. (Stenhouse.)

*Properties.* Large flat crystals which melt at 84°, and sublime in four-sided prisms at a higher temperature. Has a faint, not unpleasant odour, resembling that of sesquichloride of carbon. (Stenhouse.)

| | | | Stenhouse. |
|---|---|---|---|
| 26 C | 156·0 | 67·10 | 65·97 |
| 9 H | 9·0 | 3·87 | 3·99 |
| Cl | 35·4 | 13·77 | 16·21 |
| 4 O | 32·0 | 15·26 | 13·83 |
| $C^{26}H^{9}ClO^{4}$ | 232·4 | 100·00 | 100·00 |

It is therefore benzoate of chlorophenyl mixed with benzoate of bi- or tri-chlorophenyl. (List & Limpricht.)

Heated with alcoholic potash, it yields chloride of potassium, benzoate of potash, and a small quantity of benzoate of ethyl. Hydrochloric acid added in excess to the alkaline liquid, throws down benzoic acid and a dark-coloured resinous body, smelling of creosote. (Stenhouse.)

The liquid chlorine-compound produced by the action of chlorine on benzoate of phenyl (*vid. sup.*) may be dissolved out from the bibulous paper by ether, but it is difficult to separate from the solid compound.

| | | | Stenhouse. |
|---|---|---|---|
| 26 C | 156·0 | 51·79 | 53·43 |
| 7 H | 7·0 | 2·32 | 3·23 |
| 3 Cl | 106·2 | 35·26 | 29·59 |
| 4 O | 32·0 | 10·63 | 13·75 |
| $C^{26}H^{7}Cl^{3}O^{4}$ | 301·2 | 100·00 | 100·00 |

[It is therefore benzoate of trichlorophenyl mixed with benzoate of chlorophenyl or bichlorophenyl. The last in its pure state requires 58·43 p.c. C, 2·09 H, and 26·52 Cl. L.]

Treated with alcoholic potash, it yields chloride of potassium, benzoate of potash, and a quantity of the resinous mass larger than that which is yielded by the solid compound. (Stenhouse.)

## Benzoate of Binitrophenyl.

$C^{26}N^{2}H^{8}O^{12} = C^{12}X^{2}H^{2}O,C^{14}H^{6}O^{3}$.

LAURENT & GERHARDT. *Compt. Chim.* 1849, 429; abstr. *Ann. Pharm.* 75, 77.

*Benzoesaure Binitrocarbolsäure, benzoesaures Binitrophenyloxyd, Binitrobenzophänid.*

Crystals of binitrocarbolic acid moistened with chloride of benzoyl are gently heated, as long as they give off hydrochloric acid (longer heating would alter the product); and any binitrocarbolic acid that may have

remained unchanged, is dissolved out by dilute ammonia, washed with cold alcohol, and crystallised from boiling alcohol.

Yellow rhombic laminæ.

| | | | | Laurent & Gerhardt. |
|---|---|---|---|---|
| 26 C | 156 | | 54·17 | 54·1 |
| 2 N | 28 | | 9·72 | |
| 8 H | 8 | | 2·78 | 2·7 |
| 12 O | 96 | | 33·33 | |
| $C^{26}N^2H^8O^{12}$ | 288 | | 100·00 | |

It dissolves partially in boiling potash, forming a yellow solution.

It is insoluble in water, and nearly insoluble in boiling *alcohol.* Dissolves rather freely in warm *ether.*

## Benzoate of Trinitrophenyl.

$C^{26}N^3H^7O^{16} = C^{12}X^3H^3O,C^{14}H^5O^3.$

LAURENT & GERHARDT. *Compt. Chim.* 1849, 429; abstr. *Ann. Pharm.* 75, 77.

*Benzoesaure Trinitrocarbolsäure, benzoesaures Trinitrophenyloxyd, Trinitrobenzophänid.*

Picric acid is treated with chloride of benzoyl, as in the preparation of benzoate of binitrophenyl, and the product is washed with cold alcohol till that liquid is no longer coloured by it, and crystallised from hot alcohol.

Golden yellow rhombic laminæ, having a strong lustre. Melts when heated, and solidifies in the crystalline form on cooling.

| | | | | Laurent & Gerhardt. |
|---|---|---|---|---|
| 26 C | 156 | | 46·83 | 46·6 |
| 3 N | 42 | | 12·64 | |
| 7 H | 7 | | 2·10 | 2·1 |
| 16 O | 128 | | 38·43 | |
| $C^{26}N^3H^7O^{16}$ | 333 | | 100·00 | |

When strongly heated, it assumes a darker colour and explodes.

It dissolves in boiling potash with deep yellowish red colour and separation of crystalline flakes. — When boiled with ammonia, it remains for the most part undissolved.

It is insoluble in water, and less soluble in cold *alcohol* than benzoate of binitrophenyl. It dissolves sparingly in cold, somewhat more abundantly in warm *ether.*

## Benzolactic Acid.

$C^{40}H^{20}O^{16} = C^{12}H^{10}O^{10},2(C^{14}H^{6}O^{2})$.

SOCOLOFF & STRECKER. *Ann. Pharm.* 80, 42.
STRECKER. *Ann. Pharm.* 91, 359.

***Benzomilchsäure, Benzoemilchsäure.***

*Formation and Preparation.* Benzoic and lactic acids are heated together to 180° as long as aqueous vapour continues to escape; the solidified resinous mass is dissolved in water containing potash; dilute sulphuric acid added to the warm solution till benzoic acid no longer separates on cooling, but crystals of another form make their appearance; the precipitated benzoic acid then separated by filtration; and the filtrate treated with sulphuric acid. A copious precipitate is thereby produced, which when boiled with water, first melts and then dissolves in a larger quantity of water. As the liquid cools, the benzolactic acid is deposited either in drops or in crystals, and may be obtained in the crystalline state by solution in ether. (Socoloff & Strecker.) — ¶ Or better: 10 pts. of syrupy lactic acid are heated with 14 pts. of benzoic acid in a retort to 150°; water then passes over, a small quantity of benzoic acid sublimes, and, after the mixture has been heated for several hours to 200°, there remains a fused brownish mass, which on cooling gradually solidifies in a network of crystals consisting of benzoic and benzolactic acids. On boiling this residue with a quantity of aqueous carbonate of soda not sufficient to dissolve the whole, the benzolactic acid is dissolved in greater proportion than the benzoic acid; and the resulting solution, from which the small quantity of benzoic acid may easily be removed by agitation with ether, yields, on addition of hydrochloric acid, colourless crystals of benzolactic acid, which may be purified, by recrystallization from water, or from a mixture of ether and alcohol.

*Properties.* Colourless tabular or spear-shaped crystals, unctuous to the touch: In the dry state they melt at 112°; the fused acid remains liquid for a long time after cooling, and then solidifies in a crystalline mass. The acid does not sublime between 100° and 120°, but when strongly heated, it boils and appears to sublime unaltered. After drying in the air, it does not give off any water when heated to its melting point. (Strecker.)

| | *Air-dried.* | | Strecker. |
|---|---|---|---|
| 20 C | 120 | 61·8 | 61·6 |
| 10 H | 10 | 5·2 | 5·2 |
| 8 O | 64 | 33·0 | 33·2 |
| $C^{20}H^{10}O^{8}$ | 194 | 100·0 | 100·0 |

The acid may be regarded as $C^{14}H^{4}(C^{6}H^{5}O^{4})\left.\begin{matrix}O^{2}\\H\end{matrix}\right\}O^{2}$, that is to say, as benzoic acid in which 1 At. H within the radical (benzoyl) is replaced by lactyl $C^{6}H^{5}O^{4}$. Its formation is represented by the equation:

$$C^{12}H^{12}O^{12} + 2C^{14}H^{6}O^{4} = 2C^{20}H^{10}O^{8} + 4HO.$$

This mode of formation might lead to the conclusion that the acid is bibasic and should be represented by the formula $C^{40}H^{20}O^{16}$; but as the homologous compound benzoglycolic acid (p. 66) is monobasic, and its formula could not be doubled without doubling also the formula of hippuric acid, and therefore also that of glycocol, it is best on the whole to regard benzolactic acid as monobasic. (Strecker.)

*Decomposition.* The acid boiled with water, is very slowly resolved into benzoic and lactic acids; the decomposition is somewhat accelerated by addition of dilute sulphuric acid.

*Combinations.* The acid dissolves in 400 pts. of cold *water*, and in a smaller quantity at the boiling heat.

The *Benzolactates*, $C^{20}H^{9}MO^{6}$, are for the most part soluble in water. Their neutral solutions are not precipitated by neutral acetate of lead, a character which distinguishes benzolactic from benzoic acid.

*Benzolactate of Soda* crystallises in colourless needles.

*Benzolactate of Baryta.* — Crystallises from its aqueous solution in shining, thin six-sided laminæ. The air-dried salt gives off 17·6 p.c. (6 At.) water at 100°.

| | *At* 100°. | | | Strecker. |
|---|---|---|---|---|
| BaO | 76·5 | .... | 29·3 | 29·1 |
| $C^{20}H^{9}O^{7}$ | 185·0 | .... | 70·7 | |
| $C^{20}H^{9}BaO^{8}$ | 261·5 | .... | 100·0 | |

*Benzolactate of Silver.* — An ammoniacal solution of benzolactic acid mixed with nitrate of silver forms a flocculent precipitate, which dissolves in boiling water and crystallises in slender colourless needles on cooling.

| | | | | Strecker. |
|---|---|---|---|---|
| $C^{20}H^{9}O^{8}$ | 193 | .... | 64·5 | |
| Ag | 108 | .... | 35·5 | 36·1 |
| $C^{20}H^{9}AgO^{8}$ | 301 | .... | 100·0 | |

Socoloff & Strecker found 37 per cent. of silver in the salt, the excess arising probably from admixture of benzoic acid with the benzolactic.

The acid dissolves readily in *alcohol* and *ether*. (Strecker.) ¶.

*Secondary Nuclei of Benzylene.*

*Oxygen-nucleus* $C^{14}H^{5}O$.

## Anhydrous Benzoic Acid.

$C^{14}H^{5}O^{3} = C^{14}H^{5}O,O^{2}$.

GERHARDT. *N. Ann. Chim. Phys.* 37, 299; *Ann. Pharm.* 82, 127; 87, 163; *J. pr. Chem.* 61, 280.
WUNDER. *J. pr. Chem.* 61, 498.

*Benzoic Anhydride, Benzoate of Benzoyl, Benzoic Benzoate, Benzoesäure-Anhydrid, wasserfreie Benzoesäure, benzoesaure Benzoesäure, Benzoate benzoique.*

*Formation.* 1. By the action of chloride of benzoyl: (*a*) on oxalic acid, or (*b*), on alkaline benzoates (Gerhardt), and therefore also (*c*), by

the action of pentachloride of phosphorus on alkaline benzoates, the first stage of this action being the formation of chloride of benzoyl (Wunder); in like manner (*d*), by the action of protochloride of sulphur on alkaline benzoates (Heintz):

*a*. $C^4K^2O^8 + 2C^{14}H^5ClO^2 = 2KCl + 2C^{14}H^5O^3 + 2CO + 2CO^2$;
*b*. $C^{14}H^5NaO^4 + C^{14}H^5ClO^2 = NaCl + 2C^{14}H^5O^3$.
*c*. $6C^{14}H^5NaO^4 + PCl^5 = 3C^{14}H^5NaO^4 + 3C^{14}H^5ClO^2 + NaO,PO^5 + 2NaCl$.
*d*. $2C^{14}H^5NaO^4 + 3ClS = 2C^{14}H^5ClO^2 + NaCl + NaO,SO^3 + 2S$.

2. By distillation of acetic benzoate or cuminic benzoate. (Gerhardt.)

*Preparation.*—1. Perfectly dry oxalate of potash is heated with an equal weight of chloride of benzoyl, keeping the vessel in continual movement, till the odour of chloride of benzoyl is no longer perceptible. The cooled mass is suspended in cold water; the resulting chloride of potassium washed with cold water, to which a little ammonia is added for the purpose of removing any benzoic acid that may have been contained in the chloride of benzoyl; and the residue is crystallised from alcohol. (Gerhardt.)—2. When equal parts of dry benzoate of soda and chloride of benzoyl are heated in a sandbath to 130°, a clear liquid is produced, and at a temperature somewhat above 130°, chloride of potassium separates out; the cooled mass washed with cold water and solution of carbonate of soda, leaves anhydrous benzoic acid in the form of a white mass. (Gerhardt.)—3. Oxychloride of phosphorus* is gradually added to an excess of finely pounded benzoate of soda (about five times the weight of the oxychloride), best in a flask, which is kept in constant motion, so that the reaction which takes place as soon as the substances come in contact, may extend itself throughout the whole mass; the mixture is heated to 150° in an oil-bath or air-bath till it no longer smells of chloride of benzoyl; and the cooled mass is suspended in cold water, to which a small quantity of ammonia or carbonate of soda is added, to remove any chloride of benzoyl that may remain, and then washed with water. In this reaction, chloride of benzoyl is first formed and afterwards acts upon the benzoate of soda. (Gerhardt.)—4. When pentachloride of phosphorus is mixed with dry benzoate of soda, a strong evolution of heat takes place, and the mass is converted into a syrupy liquid This is heated for some time to 130°, the mass which solidifies on cooling treated with cold water, and the residue crystallised from boiling alcohol. (Wunder.) In preparing considerable quantities of anhydrous benzoic acid, the purification is best effected by distillation. Well developed crystals are obtained by leaving the fused substance to cool slowly, and decanting the still liquid portion from the solid matter. (Gerhardt.)—¶. 5. Thirty-seven grammes or rather more of perfectly dry and finely pounded benzoate of soda, are intimately mixed in a flask with 10 grammes of protochloride of sulphur; the flask well closed and left at rest for 24 hours; and the contents, which then smell of chloride of benzoyl, are heated above 130°, whereupon the mass liquefies and the odour of chloride of benzoyl disappears. The contents of the flask, when cold, are thrown into cold water, triturated therein with addition of a little

* According to Gerhardt, oxychloride of phosphorus is most advantageously prepared by distilling pentachloride of phosphorus with perfectly dry oxalic acid; the liquid distillate thus obtained consists wholly of the oxychloride:

$$PCl^5 + C^4H^2O^8 = PO^2Cl^3 + 2HCl + CO + CO^2.$$

carbonate of soda and afterwards washed with water; the residue pressed and melted in the water-bath; the fused mass treated with alcohol of about 50° till it is completely dissolved, with the exception of sulphur; and the filtrate left in a cool place till the anhydrous benzoic acid crystallises out. If the liquid separated from these crystals be mixed with hot water till the turbidity thereby produced no longer disappears, and again left to cool, it will yield an additional quantity of anhydrous benzoic acid in perfectly pure crystals. The crystals which first separate from the alcoholic solution still contain a little sulphur; but by melting them in the water-bath, decanting from the sulphur, dissolving the decanted portion in the exact quantity required of alcohol of 50°, decolorising the solution with recently ignited and washed bone-charcoal, and gradually cooling the hot-filtered solution, anhydrous benzoic acid is obtained in pure colourless crystals. (Heintz, *Pogg*, 98, 458.) ¶.

*Properties.* Acute rhombs or oblique rhombic prisms, having sometimes a slight odour of bitter almond oil. Melts at 42°, and remains fluid for a long time under water, even when agitated. Distils without decomposition at about 310°. Its fresh solution in alcohol or ether has no effect on litmus. (Gerhardt.)

| | | | Gerhardt. | Wunder. |
|---|---|---|---|---|
| 14 C | 84 | 74·32 | 74·19 | 74·35 |
| 5 H | 5 | 4·42 | 4·54 | 4·68 |
| 3 O | 24 | 21·26 | 21·27 | 20·97 |
| $C^{14}H^5O^3$ | 113 | 100·00 | 100·00 | 100·00 |

*Decompositions.* 1. When boiled with *water*, it communicates an acid reaction to the liquid, and by continued boiling it is converted into benzoic acid. — 2. *Potash-ley* converts it into benzoic acid. When heated with a small quantity of solid caustic potash, it yields benzoate of potash and benzoic acid. (Chiozza.)

$$2C^{14}H^5O^3 + KO,HO = C^{14}H^5KO^4 + C^{14}H^6O^4.$$

— 3. *Ammonia* appears not to act upon it in the cold, but on the application of heat, the anhydrous acid dissolves quickly, and the concentrated solution deposits benzamide; nevertheless, a large quantity of benzoate of ammonia remains in solution. *Aniline* does not act upon the anhydrous acid in the cold: but on applying a gentle heat, solution takes place, water separates, and the mass, as it cools, solidifies into a group of needles of benzamide. (Gerhardt.)

Anhydrous benzoic acid is insoluble in cold water, but dissolves readily in *alcohol* and *ether*.

## Anhydrous Benzo-acetic Acid.

$$C^{18}H^8O^6 = C^4H^3O^3 + C^{14}H^5O^3.$$

GERHARDT. *N. Ann. Chim. Phys.* 37, 308; *Ann. Pharm.* 87, 81; *J. pr. Chem.* 61, 288.

*Benzo-acetic Anhydride, Benzoic Acetate or Acetic Benzoate.*

*Formation and Preparation.* When chloride of acetyl is brought in contact with benzoate of soda, a very brisk action takes place, and

continues to the end without external heating. The syrupy product is washed with water and aqueous carbonate of soda, the residue shaken up with pure ether, and the solution left to evaporate at a gentle heat.

*Properties.* Heavy oil, smelling like Spanish wine. Does not change the colour of litmus.

| | | | | | Gerhardt. |
|---|---|---|---|---|---|
| 18 C | 108 | | 65·85 | | 65·94 |
| 8 H | 8 | | 4·87 | | 4·99 |
| 6 O | 48 | | 29·28 | | 29·07 |
| $C^{18}H^{8}O^{6}$ | 164 | | 100·00 | | 100·00 |

*Decompositions.* 1. The compound boils at 120°, and anhydrous acetic acid passes over, the thermometer rising rapidly, and the residue acquiring a slight brown colour. If the distillation is interrupted at 180°, the residue contains pure anhydrous benzoic acid. — 2. When boiled with water, it is slowly converted into acetic and benzoic acids. — Caustic alkalis and alkaline carbonates quickly convert it into a benzoate and an acetate of the alkali.

## Anhydrous Benzo-valeric Acid.

$C^{28}H^{14}O^{6} = C^{16}H^{9}O^{3},C^{14}H^{5}O^{3}$.

CHIOZZA. *Ann. Pharm.* 84, 106; *J. pr. Chem.* 61, 298.

*Benzo-valeric Anhydride, Valeric Benzoate, or Benzoic Valerate.*

Obtained by the action of chloride of benzoyl on dry valerate of potash.

Heavy oil having nearly the same odour as anhydrous valerianic acid. Does not change the colour of litmus. Emits pungent vapours which excite tears. It is resolved by distillation into anhydrous benzoic and valerianic acids, but not so readily as anhydrous benzo-acetic acid. With alkalis it forms a benzoate and a valerate.

*Appendix to Anhydrous Benzoic Acid.*

## Oreoselone. $C^{14}H^{5}O^{3}$.

SCHNEDERMANN & WINCKLER. *Ann. Pharm.* 51, 320.

*Preparation.* A rapid stream of dry hydrochloric acid is passed over finely pulverised athamantin, the powder being continually stirred, so that every part of it may be exposed to the action of the acid (p. 103). When the whole is liquefied and begins to solidify again, the heat is raised to 100°; hydrochloric and valerianic acids then pass over, and oreoselone (mixed with unaltered athamantin) remains as an amorphous porous

mass. This product is recrystallised from boiling alcohol; and the solution, when cooled or evaporated, deposits oreoselone in yellowish nodules, which, by washing with cold alcohol, are rendered whiter, and are freed from adhering athamantin. — Sulphurous acid may also be used in the preparation instead of hydrochloric acid.

*Properties.* Loosely coherent, cauliflower-like mass, which, when examined with a magnifying glass, appears to be composed of slender flexible needles arranged in spherical groups. It has a faint yellowish colour (which however arises merely from impurity, inasmuch as oreoselone undergoes alteration when its solution is evaporated). Tasteless and inodorous. Melts at about 190° into a clear yellow liquid.

| | | | Schnedermann & Winckler. |
|---|---|---|---|
| 14 C | 84 | 74·32 | 74·79 |
| 5 H | 5 | 4·42 | 4·59 |
| 3 O | 24 | 21·26 | 20·62 |
| $C^{14}H^5O^3$ | 113 | 100·00 | 100·00 |

*Decompositions.* Fused oreoselone solidifies on cooling, into an amber-coloured mass, which again separates in the amorphous state from its solutions; when melted, it emits a slight empyreumatic odour, without however diminishing in weight. When heated above its melting point, it becomes charred. — 2. Oreoselone dissolves readily in *oil of vitriol*, and the solution, on being mixed with water, yields a copious yellowish white precipitate, which, after washing and drying, forms a yellowish powder, soluble with yellow colour in potash and in alcohol; it does not however crystallise from its alcoholic solution, and it contains less carbon and more hydrogen than oreoselone. — 3. Oreoselone turns yellow when treated with dilute potash or ammonia, and dissolves to a small amount, forming a solution of a bright yellow colour; *strong potash-ley* with the aid of heat, dissolves it abundantly. The red-brown solution yields with acids a yellowish white precipitate, which, after washing and drying, forms a yellowish earthy mass, becoming brownish and glutinous when dry (especially if it has been prepared from athamantin not quite pure); it dissolves with some difficulty in water, and (if prepared from oreoselone) remains in the form of a crystalline mass when the alcoholic solution is evaporated. By repeated solution and evaporation, it becomes darker in colour and more readily soluble in alcohol. It contains 72·21 p. c. carbon and 4·72 hydrogen, and is therefore a hydrate of oreoselone containing however less than 1 At. water. [The amount of hydrogen and oxygen, is however greater as compared with oreoselone, not in the ratio of 1 : 8, but of 1 : 11; the substance is therefore nothing but oreoselone somewhat decomposed. L.]

*Combinations.* The precipitate recently thrown down by acids from the solution of oreoselone in potash dissolves readily in ammonia, forming an alkaline liquid, from which neutral acetate of lead throws down yellow flakes. This precipitate, even when every precaution is adopted in its preparation, to avoid any admixture of carbonate or basic acetate of lead, exhibits a composition varying in different preparations, but nevertheless approaching to the formula $C^{14}H^5O^3,2PbO$.

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | Schnedermann & Winckler. | | |
| 2 PbO | 223·6 | .... | 66·36 | ..... | 66·54 | .... | 65·80 | .... | 64·44 | .... | 61·27 |
| 14 C | 84·0 | .... | 25·02 | ..... | 24·59 | .... | 25·13 | .... | 26·12 | .... | 28·24 |
| 5 H | 5·0 | .... | 1·48 | ..... | 1·71 | .... | 1·62 | .... | 1·79 | .... | 2·08 |
| 3 O | 24·0 | .... | 7·14 | ..... | 7·16 | .... | 7·45 | .... | 7·65 | .... | 8·41 |
| $C^{14}H^{5}O^{3},2PbO$ | 336·6 | .... | 100·00 | ..... | 100·00 | .... | 100·00 | .... | 100·00 | .... | 100·00 |

Oreoselone dissolves but sparingly in *alcohol*, even when warm, forming a yellow solution, and to about the same extent in *ether*.

*Body obtained from Hydrochlorate of Athamantin.* $C^{14}H^{8}O^{4}$.

The crystallised compound of athamantin and hydrochloric acid melts, when boiled with water, into oily drops which dissolve after boiling for some time. The liquid on cooling deposits slender needles, forming, when dried, a dazzling white silky mass, which dissolves sparingly in cold, pretty readily in boiling water, easily in alcohol or ether, and separates in small scaly crystals from the alcoholic solution, in slender needles from the ethereal solution. The same body is sometimes also produced on boiling the crude mass of athamantin which has been treated with hydrochloric acid; sometimes however nothing separates under these circumstances, but oreoselone and a few amorphous flakes which pass over in distillation together with the liquid. The compound dissolves with yellow colour in ammonia and more readily in dilute potash-ley, and is precipitated by acid from the dilute solution in slender colourless crystals. The solution in ammonia, forms a beautiful yellow precipitate with acetate of lead.

| | | | | | |
|---|---|---|---|---|---|
| | | | | | Schnedermann & Winckler. |
| 14 C | 84 | .... | 68·85 | ..... | 69·05 |
| 6 H | 6 | .... | 4·91 | ..... | 5·02 |
| 4 O | 32 | .... | 26·24 | ..... | 26·93 |
| $C^{14}H^{6}O^{4}$ | 122 | .... | 100·00 | ..... | 100·00 |

The compound melts when heated in a glass tube; at a stronger heat the liquid creeps up the sides of the tube, and forms a brownish oil, which does not solidify till after some days. At the same time, a slight empyreumatic odour is emitted and a small quantity of charcoal separates.

## Peucedanin.

$$C^{24}H^{12}O^{6} = C^{14}H^{5}O^{3},C^{10}H^{7}O^{3}.$$

WACKENRODER. *Br. Arch.* 37, 341.
SCHLATTER. *Ann. Pharm.* 5, 201.
ERDMANN. *J. pr. Chem.* 16, 42.
BOTHE. *J. pr. Chem.* 46, 371; 50, 381.
R. WAGNER. *J. pr. Chem.* 61, 503; 62, 275.

*Angelate of Oreoselone, Imperatorin.*

*Sources.* In the root of *Peucedanum officinale* (sulphur weed) and *Imperatoria Astruthium* (masterwort). R. Wagner has shown that

Wackenroder's imperatorin is identical with the peucedanin discovered by Schlatter.

*Preparation.* 1. When the root of *Peucedanum officinale* is exhausted by digestion with alcohol of 80 per cent. and the alcohol afterwards distilled off, peucedanin separates from the fatty residue in crystals which may be washed with cold, and recrystallised from hot alcohol. (Schlatter.) Herberger and Erdmann recrystallise the product from ether. Bothe leaves the comminuted root in contact with alcohol for some hours and then heats the liquid to the boiling point; the filtered liquid, when slightly evaporated, yields crystals of peucedanin, which may be freed from a brown resin by treating them with cold and very dilute alcohol. The crystallisations from subsequent extracts contain much larger quantities of resin than that obtained from the first; from the last quantities of resin, the peucedanin may be obtained by diluting the hot alcoholic solution with water, till the turbidity thereby produced begins to be permanent; the crystals which separate after long standing are recrystallised from cold ether. (Bothe.)

2. The coarsely pounded root of *masterwort* is exhausted in a press with 2 or 3 pts. of ether, $\frac{1}{4}$ of the liquid distilled off, and the residue exposed to the air, whereupon it deposits crystals, which must be separated from a green oil and recrystallised from ether. To free them completely from adhering oil, they are washed with cold alcohol of 80 per cent. and recrystallised from hot alcohol, or melted at a gentle heat and recrystallised, or left for some hours in contact with cold dilute potash, then washed first with water, afterwards with cold alcohol, and recrystallised from hot alcohol. (Osann, Wackenroder.) — Wagner exhausts old roots of masterwort (the fresh roots do not appear to yield any peucedanin) with alcohol of 75 per cent. at ordinary temperatures; concentrates the extract at about 60°, till it separates on being left at rest into two layers, the lower of which is light brown and watery, the upper brown and resinous; spreads the latter upon a porcelain dish and leaves it to itself for some days; presses the resulting granular crystalline mass between bibulous paper (to remove a fixed oil resembling linseed oil); boils it with milk of lime; decomposes the resulting lime-compound with acetic acid (whereby the product is freed from a substance which gives it a burning taste); and recrystallises the peucedanin thus separated from cold alcohol.

*Properties.* Colourless, shining rhombic tables destitute of taste and smell (Schlatter, Bothe), with angles of about 60° and 120°; thick, oblique rhombic prisms with terminal faces resting obliquely on the obtuse lateral edges (Wackenroder); the alcoholic solution has a burning, aromatic taste, and produces a persistent sensation of scratching in the throat. Melts at 60° (Schlatter), at 75° (Bothe, Wackenroder), and when left at rest for some time, solidifies in a radiated crystalline mass.

| | | | Erdmann. | Bothe. | Wagner. |
|---|---|---|---|---|---|
| 24 C | 144 | 70·58 | 69·69 | 70·53 | 70·13 |
| 12 H | 12 | 5·88 | 5·88 | 6·02 | 6·33 |
| 6 O | 48 | 23·54 | 24·43 | 23·45 | 23·54 |
| $C^{24}H^{12}O^{6}$ | 204 | 100·00 | 100·00 | 100·00 | 100·00 |

*Decompositions.* 1. Peucedanin heated above its melting point, gives off vapours having a rancid aromatic odour and producing a scratching sensation in the throat; they condense into an unctuous mass which solidifies as it cools. It burns with a bright sooty flame and leaves a light charcoal difficult to burn.—2. Heated to 60° with nitric acid of sp. gr. 1·21, it dissolves slowly but completely, forming a yellow liquid, which on cooling solidifies into a laminar crystalline mass of *nitropeucedanin*. This compound is easily purified by recrystallisation from alcohol, and forms colourless flexible crystalline laminæ, which are nearly insoluble in water, dissolve with tolerable facility in alcohol and ether, melt and decompose when heated above 100°, and burn with a bright flame, giving off nitrous vapours. (Bothe.)

| *Nitropeucedanin.* | | | Bothe. |
|---|---|---|---|
| 24 C | 144 | 60·01 | 59·47 |
| N | 14 | 5·83 | 5·25 |
| 10 H | 10 | 4·16 | 4·11 |
| 9 O | 72 | 30·00 | 31·17 |
| $C^{24}NH^{10}O^{9}$ | 240 | 100·00 | 100·00 |

Nitropeucedanin exposed to the action of ammoniacal gas or heated with ammonia and alcohol, is converted into *nitropeucedamide*, which dissolves readily in boiling alcohol, and crystallises on cooling in rhombic prisms having almost the lustre of the diamond.

| *Nitropeucedamide.* | | | Bothe. |
|---|---|---|---|
| 24 C | 144 | 58·06 | 58·00 |
| 2 N | 28 | 11·29 | 11·92 |
| 12 H | 12 | 4·84 | 4·63 |
| 8 O | 64 | 25·81 | 25·45 |
| $C^{24}N^{2}H^{12}O^{8}$ | 248 | 100·00 | 100·00 |

Nitropeucedamide boiled with potash gradually gives off ammonia; heated with a dilute acid, it yields nitropeucedanin and the ammonia-salt of the acid employed.

Nitropeucedamide is nearly insoluble in water, but dissolves readily in alcohol and ether. When the alcoholic solution is mixed with water, the precipitated nitropeucedamide exhibits a remarkable dichroism, the liquid being yellow by transmitted light, but of a fine azure-blue by reflected light, even when very much diluted. (Bothe.)

When peucedanin is boiled with strong nitric acid, nitrous acid is evolved and a yellow solution formed which is not precipitated by water. (Schlatter, Weckenroder.)

3. Peucedanin forms a dark viscid mass with *iodine*. (Schlatter, Wackenroder.)—4. It dissolves in *oil of vitriol* and is precipitated in its original state by water, but is slightly altered by fuming sulphuric acid. (Wackenroder.) Sulphuric, hydrochloric and acetic acid have no action on peucedanin. (Schlatter.)—5. It is decomposed by alcoholic potash into angelic acid and oreoselone. (R. Wagner.)

Peucedanin is insoluble in water and very sparingly soluble in cold alcohol, but dissolves readily in hot *alcohol*, in *ether*, and in *oils* both *fixed* and *volatile*.

When peucedanin is dissolved in cold ether, *oxypeucedanin* remains in the form of a granular residue, which may be freed from adhering peucedanin by repeated crystallisation and treatment with ether. (Erdmann, Bothe.)

| | *Oxypeucedanin.* | | Bothe. |
|---|---|---|---|
| 24 C | 144 | 68·25 | 67·80 |
| 11 H | 11 | 5·21 | 5·27 |
| 7 O | 56 | 26·54 | 26·93 |
| $C^{14}H^{11}O^{7}$ | 331 | 100·00 | 100·00 |

## Athamantin.

$C^{24}H^{16}O^{7} = C^{14}H^{6}O^{3},C^{10}H^{10}O^{4}$ or $C^{14}H^{6}O^{4},C^{10}H^{9}O^{3}$. ?

WINCKLER. *Repert.* 77, 169.
SCHNEDERMANN & WINCKLER. *Ann. Pharm.* 51, 315; *J. pr. Chem.* 33, 39.

*Preparation.* The dried and finely bruised roots and ripe seeds of *Athamanta oreoselinum* are exhausted with three times their weight of alcohol of 80 per cent. at 50° or 60°; the solution evaporated to dryness over the water-bath; the residue treated with eight times the quantity of ether; and the ethereal solution decolorised with animal charcoal, filtered and left to evaporate: there then remains a thickish pale yellowish oil which gradually solidifies into a crystalline granular mass. This mass is dissolved in four times its weight of 80 per cent. alcohol; 60 times the weight of water poured into the solution in a thin stream; and the mixture well shaken and left to stand in a cool place. The milky liquid after a few days or perhaps weeks, deposits a curdy crystalline precipitate; the addition of acetic acid or sulphate of soda accelerates the precipitation, but retards the subsequent purification. The precipitate is dissolved in a quantity of warm alcohol of 60—63 per cent., sufficient to keep the liquid nearly clear after cooling, then filtered warm and left to stand in a cool place. The athamantin then separates in long needles, generally mixed with oily drops of impure athamantin. From a solution saturated while warm, athamantin separates on cooling in the form of a brown oil. The crystalline mass freed as completely as possible from the oil-drops, is pressed between bibulous paper, and recrystallised from alcohol till the crystals appear perfectly white and are no longer mixed with oil.

The very loosely coherent, dazzling white, satiny mass consisting of interlaced capillary flexible crystals, very like long-fibred asbestos, which is thus obtained, is not yet pure athamantin, inasmuch as it melts at a lower temperature (between 59° and 60°) and contains more carbon and hydrogen (68·8 p. c. C and 7·5 p. c. H). Pure athamantin cannot be obtained from it by recrystallisation; it is sometimes accidentally obtained in large crystals which separate at the same time as the fine needles, or when the oily mass separated from the alcoholic solution is left for some time in contact with the supernatant liquid at 20°.

*Properties of pure Athamantin.* — Colourless rectangular prisms, sometimes an inch long, with truncated summits, two of the truncation-

faces lying opposite to each other being much larger than the other two; sometimes octohedrons having four of their summits in the same plane truncated. Has a peculiar rancid soapy odour, especially when heated, and a rancid, somewhat bitter taste, leaving a slight scratching sensation in the throat. Melts at about 79°, and forms on cooling a white mass of the consistence of turpentine, which after a while solidifies in radiated masses resembling wavellite. Cannot be distilled without decomposition.

| | | | Schnedermann & Winckler. |
|---|---|---|---|
| 24 C | 144 | 66·98 | 66·78 |
| 15 H | 15 | 6·98 | 6·97 |
| 7 O | 56 | 26·04 | 26·25 |
| $C^{24}H^{15}O^{7}$ | 215 | 100·00 | 100·00 |

If we suppose, with Schnedermann & Winckler, that athamantin contains anhydrous valerianic acid associated with the body $C^{14}H^{6}O^{4}$, this body must be regarded as derived from the nucleus $C^{14}H^{5}O^{3}$ (Oreoselone ?), and athamantin as analogous to the compound ethers: $C^{14}H^{5}O^{3},HO + C^{10}H^{9}O^{3}$; on this supposition athamantin treated with hydrochloric acid, should yield a compound of $C^{14}H^{5}O^{3},HCl$ with $C^{10}H^{10}O^{4}$, which when heated, would resolve itself into oreoselone, hydrochloric acid and valerianic acid. But in that case, athamantin, when treated with potash, should yield a body analogous to alcohol, viz., $C^{14}H^{5}O^{3},2HO$, whereas the product of this reaction is merely $C^{14}H^{6}O^{4}$.—If athamantin be regarded as a conjugated compound of oreoselone and valerianic acid = $C^{14}H^{5}O^{3},C^{10}H^{10}O^{4}$, the decomposition by potash is at once explained, since the body $C^{14}H^{6}O^{4}$ may be regarded as the hydrate of oreoselone; against this view however, it must be alleged that the formation of this compound is not attended, as it should be (p. 221), with formation of water.

*Decompositions.* 1. Athamantin subjected to *dry distillation*, yields a large quantity of valerianic acid together with other products.—2. With *nitric acid* of 1·25 in the cold, it yields a colourless oil which floats on the surface of the liquid, and after a while becomes turbid and smells of valerianic acid. On heating the liquid, nitrous fumes are evolved, and the odour of valerianic acid becomes stronger, and at the time an insoluble substance separates, having the odour of fat decomposed by nitric acid.—3. With *iodine*, athamantin assumes a yellowish brown colour and yields a dark brown gummy mass smelling of valerianic acid.—4. It dissolves in *oil of vitriol*, with rise of temperature, forming a clear brownish liquid, while a powerful odour of valerian is emitted; if the heat be kept down by external cooling, the solution acquires but little colour. On mixing the solution with water, a precipitate is formed consisting of oreoselone more or less altered by oil of vitriol. On distilling the liquid, aqueous valerianic acid passes over, rendered turbid by a flocculent substance which floats in it, and appears to be identical with the body $C^{14}H^{6}O^{4}$.—5. Heated in *sulphurous* or *hydrochloric acid gas*, or boiled with aqueous hydrochloric acid, it is resolved into oreoselone and valerianic acid.—When hydrochloric acid gas is passed into the alcoholic solution, valerianic ether and oreoselone are produced.—6. *Potash* decomposes it into valerianic acid and oreoselone, which, by the further action of potash, is converted into the body $C^{14}H^{6}O^{4}$. A similar decomposition is produced, though much less quickly, by *baryta-water* and *milk of lime*.

*Combinations.* 1. In a current of dry *sulphurous acid gas*, athamantin melts at ordinary temperatures, slowly but completely, into a clear yellow-brownish oil, which generally decomposes after a few hours,

oreoselone being separated in small crystals, and a strong odour of sulphurous and valerianic acids being given off. The oil often remains apparently unaltered for several days, and then solidifies into a crystalline mass which melts when heated; but if the body be cooled with ice during the action of the sulphurous acid, and the fluid mass afterwards kept cool with ice, small crystalline stars separate, after a while, and ultimately cover the entire mass with a solid crust, while a portion remains fluid for some time longer. The crystallised mass is waxy and dry, diminishes gradually in weight in consequence of the escape of sulphurous and valerianic acids, and melts below 100°, but is decomposed by heat, oreoselone separating out, while sulphurous and valerianic acids are given off. It dissolves readily in alcohol, and appears to remain unaltered when the alcohol is left to evaporate spontaneously; but if the evaporation be assisted by heat, valerate of ethyl is produced and oreoselone remains behind. — Athamantin over which sulphurous acid gas is passed, takes up 14·63 $SO^2$ (1 At.). — 2. *Hydrochloric acid gas* is absorbed by athamantin without perceptible rise of temperature, producing a clear yellow-brown oil, which soon begins to solidify, with formation of white needles arranged in radiated groups; a portion often solidifies before the liquefaction of the whole is complete, and thereby hinders the complete transformation. The solidified mass consists, partly of needles united in stellate groups, and is partly amorphous, grey, moist, and smells strongly of valerianic acid; it gives off that acid indeed, even when preserved in close vessels. When shaken up with ether, it left a metallic powder, which, after rinsing with a small quantity of ether, was found to consist of pearly microscopic plates, easily soluble in alcohol and ether, and consisting of a compound of athamantin and hydrochloric acid.

| | | | Schnedermann & Winckler. |
|---|---|---|---|
| $C^{24}H^{15}O^7$ | 215·0 | 85·52 | |
| ClH | 36·4 | 14·48 | 13·70 |
| $C^{24}H^{15}O^7$,ClH | 251·4 | 100·00 | |

The compound has but little stability and was only once obtained by Schnedermann & Winckler in a satisfactory state of purity. The ethereal solution left on evaporation needle-shaped crystals and a mass having the appearance of oreoselone; when the solution was evaporated by heat, the residue consisted entirely of oreoselone. It melted below 100° into a liquid which gave off bubbles of hydrochloric acid and gradually changed into oreoselone. When boiled with water, it yielded the body $C^{14}H^6O^4$ (p. 98).

Athamantin is insoluble in water, but dissolves readily in *alcohol* even dilute, and in *ether;* abundantly also in *oil of turpentine* and in *fixed oils.*

## ¶. *Oxygen-nucleus* $C^{14}H^4O^2$.

*Conjugated Compounds.*

### Monobenzoïcin.

$C^{20}H^{12}O^6 = C^{14}H^4O^2,C^6H^8O^6$.

BERTHELOT. *N. Ann. Chim. Phys.* 41, 290.

*Monobenzoate of Glycerin, Monobenzoate of Glycyl.*

*Preparation.* By heating a mixture of benzoic acid and glycerin in a sealed tube for 44 hours, either to between 120° and 150° with the acid in excess, or to 200° with the glycerin in excess, — or to 275° for 5 to 20 hours. — At 100°, only a few drops are obtained after 140 hours. At ordinary temperatures, traces are formed in three months. The product is purified by washing with carbonate of potash. — The liquid then separates into two layers (as in the preparation of acetin, ix, 497), both of which are insoluble in ether. The upper layer left to evaporate in vacuo for several days exhibits traces of crystallisation; it forms an emulsion with water, and when heated yields a considerable quantity of alkaline ash. These phenomena appear to indicate the existence of a benzoglycerate of potash.

*Properties.* Colourless, neutral, very viscid oil, having a bitter and aromatic taste, and a slight balsamic odour, especially when heated. Sp. gr. 1·228 at 16·5°. At —40°, it forms a transparent, nearly solid, resinous mass, capable of being drawn into long threads. Begins to boil at 320°, but decomposes at the same time.

| | | | | Berthelot. | | | |
|---|---|---|---|---|---|---|---|
| | | | | *a.* | *b.* | *c.* | *d.* |
| 20 C | 120 | 61·2 | | 59·8 | 61·0 | 61·9 | 61·7 |
| 12 H | 12 | 6·1 | | 6·1 | 5·7 | 6·2 | 6·7 |
| 2 O | 16 | 32·7 | | 34·1 | 33·3 | 31·9 | 31·6 |
| $C^{20}H^{12}O^2$ | 148 | 100·0 | | 100·0 | 100·0 | 100·0 | 100·0 |

*a*, was prepared at 150°, with excess of acid; *b* at 200° with excess of glycerin; *c* and *d*, at 275°.

*Decompositions.* 1. Monobenzoïcin oxidises but very slightly when exposed to the air. — 2. When boiled, it is decomposed, giving off acrolein, and a considerable quantity of benzoic acid, exhaling at the same time an odour similar to that which is evolved in the distillation of castor oil. — 3. Heated with caustic potash, it yields benzoate of potash. — 4. Ammonia converts it into benzamide. — 5. Treated in the cold with alcohol and hydrochloric acid it yields glycerin and benzoate of ethyl. The same transformation is produced by heating an alcoholic solution of monobenzoicin to 100° for 48 hours. The same alcoholic solution acquires the odour of benzoic ether when merely exposed to the air; but in a closed vessel it remains unaltered.

*Combinations.* Monobenzoïcin is insoluble in water, and nearly or quite insoluble in bisulphide of carbon, but dissolves with great facility in *alcohol, ether*, and *benzol.*

*Derivative of Monobenzoïcin.*

## Benzochlorhydrin.

$C^{20}H^{11}ClO^6 = C^{14}H^8Cl,C^6H^5O^6$.

BERTHELOT. *N. Ann. Chim. Phys.* 41, 302.

Obtained by saturating with hydrochloric acid gas a mixture of glycerin and benzoic acid kept for several hours at 100°, and removing the excess of acid after some time by means of carbonate of soda.

$$C^{14}H^6O^4 + HCl + C^6H^6O^6 = C^{20}H^{11}ClO^6 + 4HO.$$

Neutral oil, which solidifies at —40°, but resumes the liquid form as soon as the temperature rises.

| | | | | Berthelot. |
|---|---|---|---|---|
| 20 C | 120·0 | 56·1 | | 56·4 |
| 11 H | 11·0 | 5·1 | | 5·4 |
| Cl | 35·4 | 16·6 | | 17·0 |
| 6 O | 48·0 | 22·2 | | 21·2 |
| $C^{20}H^8ClO^6$ | 214·4 | 100·0 | | 100·0 |

May be regarded as monobenzoïcin in which $HO^2$ is replaced by Cl,—or as a conjugated compound of the chlorine-nucleus $C^{14}H^8Cl$, derived from the primary nucleus $C^{14}H^4$.

Benzochlorhydrin treated with potash yields chloride of potassium and benzoate of potash.—With hydrochloric acid and alcohol, it forms glycerin and benzoate of ethyl.—Heated with oxide of silver to 100°, it does not yield any chlorhydrin (ix, 498), even after a considerable time. When it is heated with margaric acid to 240° for four hours, the latter appears to enter into the neutral compound.

## Tribenzoïcin.

$C^{48}H^{30}O^{12} = (C^{14}H^4O^2)^3,C^6H^5O^6$.

BERTHELOT. *N. Ann. Chim, Phys.* 41, 293.

*Terbenzoate of Glycerin, Terbenzoate of Glycyl.*

Obtained by heating monobenzoïcin, for four hours to 250° with 10 or 15 times its weight of benzoïc acid. On removing the excess of acid by carbonate of soda, extracting with ether, and evaporating the ether over the water-bath, a nearly solid resinous mass is obtained, which when redissolved in ether and treated with animal charcoal, yields by evaporation in vacuo, small crystals grouped in velvety tufts. These crystals are pressed and redissolved in ether, and the solution is left to evaporate

in a bottle having its mouth covered with a sheet of paper. The compound is thus obtained in large, white, beautiful needles, which are neutral, unctuous to the touch, and fuse pretty readily. Treated with hydrochloric acid and alcohol, they yield glycerin and benzoate of ethyl.

| | | | Berthelot. |
|---|---|---|---|
| 48 C | 288 | 71·3 | 71·9 |
| 20 H | 20 | 5·0 | 5·4 |
| 12 O | 96 | 23·7 | 22·7 |
| $C^{48}H^{20}O^{12}$ | 404 | 100·0 | 100·0 |

According to the radical theory, glycerin is a triatomic alcohol, formed from three molecules of water, $H^6O^6$ or $\begin{matrix}HHO^2\\HHO^2\\HHO^2\end{matrix}$, by the substitution of the triatomic radical $C^6H^5$ for $H^3$, so that its formula may be written $\begin{matrix}H & O^2\\H(C^6H^5) & O^2\\H & O^2\end{matrix}$. Each of the three remaining atoms of hydrogen may be replaced by other radicals positive or negative. *Monobenzoïcin*, is formed by the substitution of the radical benzoyl ($C^{14}H^5O^2$ = Bz) for 1 At. H; it is therefore $\begin{matrix}Bz & O^2\\H(C^6H^5) & O^2\\H & O^2\end{matrix}$. The replacement of a second atom of hydrogen in the same manner would give *bibenzoïcin* $\begin{matrix}Bz & O^2\\Bz(C^6H^5) & O^2\\H & O^2\end{matrix}$ or $C^{34}H^{16}O^{10}$, a compound not yet obtained; and the similar replacement of the third atom of hydrogen by benzoyl, gives *tribenzoïcin*, $Bz^3(C^6H^5)O^6$. *Benzochlorhydrin*, as already observed (p. 105), may be derived from monobenzoïcin by the substitution of Cl for $HO^2$, making its formula $\begin{matrix}Bz & O^2\\H(C^6H^5) & O^2\\Cl\end{matrix}$. Similarly for the acetins, valerins, &c. (ix, 496; x, 92; xii, 75; see also Wurtz. *N. Ann. Chim. Phys.* 43, 492). ¶.

*Sulphur-nucleus* $C^{14}SH^5$.

## Sulphide of Benzoyl.

$C^{14}SH^5O^2 = C^{14}SH^5,O^2$.

Wöhler & Liebig. (1832.) *Ann. Pharm.* 3, 267; also *Pogg.* 26, 342.

*Schwefelbenzoyl, Schwefelbenzaldid, Benzoebiacisulfid, Oxyschwefelbenzoyl.*

When chloride of benzoyl is distilled with finely pulverised sulphide of lead, a yellow oil passes over, which solidifies into a soft yellow crystalline mass having an unpleasant odour of sulphur. — It burns with a bright sooty flame, giving off sulphurous acid. It does not appear to be decomposed by boiling with water. When boiled with aqueous potash, it very slowly yields benzoate of potash and sulphide of potassium. It does not decompose in contact with alcohol.

*Iodine-nucleus* $C^{14}IH^{5}$.

## Iodide of Benzoyl.

$C^{14}IH^{5}O^{2} = C^{14}IH^{5},O^{2}$.

WÖHLER & LIEBIG. (1832.) *Ann. Pharm.* 3, 267; also *Pogg.* 26, 432.

*Iodbenzoyl, Iodbenzaldid, Benzoebiacliodid, Oxyiodbenzoyl.*

When chloride of benzoyl is heated with iodide of potassium, a brown liquid passes over, which solidifies into a crystalline mass coloured brown by free iodine.—In the pure state it is colourless and lamino-crystalline, and fuses readily, but with incipient decomposition, giving off vapours of iodine. In odour and combustibility, and in its reactions with water and alcohol, it resembles bromide of benzoyl.

*Bromine-nucleus* $C^{14}BrH^{5}$.

## Bromide of Benzoyl.

$C^{14}BrH^{5}O^{2} = C^{14}BrH^{5},O^{2}$.

WÖHLER & LIEBIG. *Ann. Pharm.* 3, 266; also *Pogg.* 26, 341.

*Brombenzoyl, Brombenzaldid, Benzoebiacibromid, Oxybrombenzoyl.*

*Preparation.* When pure bitter almond oil is mixed with bromine, the mixture becomes heated and gives off hydrobromic acid, which, together with the excess of bromine, may be completely removed by heating the liquid.

*Properties.* Soft, broadly laminar crystalline mass, having a brownish colour, and, semifluid at ordinary temperatures; smells like chloride of benzoyl, but much fainter and somewhat more aromatic.—Fumes in the air, slightly at ordinary temperatures, strongly when heated. Melts even at a very gentle heat, forming a brownish yellow liquid.

It burns with a bright sooty flame. Decomposes very slowly in contact with water, and when heated under water, remains at the bottom for a long time in the form of a brownish oil, being decomposed only after long boiling into hydrobromic and benzoic acids.

It dissolves readily and without decomposition in *alcohol* and *ether*, and remains in the crystalline state when the solution is evaporated.

## Bromobenzoic Acid.

$C^{14}BrH^{5}O^{4} = C^{14}BrH^{5},O^{4}$,

PELIGOT. (1836.) *Compt. rend.* 32, 11; also *J. pr. Chem.* 7, 330; 8, 65.
HERZOG. *N. Br. Arch.* 23, 16.
MÜLLER. *Compt. rend.* 30, 325.

*Formation and Preparation.* 1. Benzoic acid together with bromine is exposed to sunshine in a closed vessel. The action is stronger and

comes to an end sooner than that of chlorine on benzoic acid. The hard friable mass which remains after the excess of bromine has been driven off, dissolves in carbonate of potash, with separation of a greenish oil containing bromine, which hardens when exposed to the air and smells like gum benzoin; the solution is decolorised by animal charcoal and precipitated by nitric acid. (Herzog.) — 2. Bromine vapour is made to act gradually upon benzoate of silver, by introducing from 20 to 24 grammes of benzoate of silver and an open tube containing liquid bromine into a stoppered glass vessel, and leaving the vessel closed for 24 hours. When liquid bromine is poured upon benzoate of silver, a violent action takes place. If the resulting mixture of bromide of silver and bromobenzoic acid be shaken up with ether, alcohol or wood-spirit, and the solution left to evaporate, an oil is left which solidifies in a crystalline mass on cooling. (Peligot.) — Müller heats benzoate of silver with bromine, whereupon benzoic acid distils over.

*Properties.* Colourless, hard, crystalline mass, which melts at 100°, and sublimes at 250°. It burns with a green-edged flame. — The acid precipitated by water from the alcoholic solution has less lustre when dry than benzoic acid. (Peligot.)

*Combinations.* With bases, the acid forms crystallisable salts, most of which dissolve very readily in water; the lime, baryta, cupric and mercurous salts are however less soluble. The *lead-salt* obtained by precipitating neutral acetate of lead with bromobenzoate of potash forms yellow crystalline grains; its solution in warm water yields by spontaneous evaporation, yellow bulky crystals apparently of spherical shape. — The silver-salt is soluble in warm water.

| | | | | Peligot. |
|---|---|---|---|---|
| 14 C | 84·0 | 27·27 | | 27·13 |
| Br | 80·0 | 25·98 | | 25·52 |
| Ag | 108·1 | 35·07 | | 34·48 |
| 4 H | 4·0 | 1·30 | | 1·46 |
| 4 O | 32·0 | 10·38 | | 11·41 |
| $C^{14}BrH^{4}AgO^{4}$ | 308·1 | 100·00 | | 100·00 |

According to Müller, bromobenzoic acid = $C^{14}Br^{1}H^{5}O^{4}$.

The acid dissolves sparingly in *water*, readily in *wood-spirit, alcohol* and *ether*.

*Chlorine-nucleus* $C^{14}ClH^{5}$.

## Chloride of Benzoyl.

$C^{14}ClH^{5}O^{2} = C^{14}ClH^{5},O^{2}$.

WOHLER & LIEBIG. *Ann. Pharm.* 3, 262; also *Pogg.* 26, 237.
CAHOURS. *Compt. rend.* 22, 846; also *Ann. Pharm.* 60, 251. — *Compt. rend.* 25, 724.
GERHARDT. *N. Ann. Chim. Phys.* 37, 291; also *Ann. Pharm.* 87, 63.

*Oxide of Chlorobenzylene, Chlorbenzoyl, Chlorbenzaldid, Benzoylchlorid, Oxychlorobenzoyl, Chlorure de benzoile.*

*Formation.* 1. By the action of chlorine on bitter almond oil. (Wöhler & Liebig.)

$$C^{14}H^6O^2 + 2Cl^2 = C^{14}ClH^5O^2 + HCl.$$

2. By the action of chlorine on benzoate of methyl or benzoate of ethyl (Malaguti, *Ann. Chim. Phys.* 70, 374 and 387), and on cinnamein. (Fremy, *Ann. Chim. Phys.* 70, 180.) — 3. By heating pentachloride of phosphorus with benzoic acid. (Cahours.)

$$C^{14}H^6O^4 + PCl^5 = C^{14}ClH^5O^2 + PCl^3O^2 + HCl.$$

— 4. By the action of oxychloride (or pentachloride) of phosphorus on benzoates. (Gerhardt.) — 5. By the action of protochloride of sulphur on alkaline benzoates. (Heintz, p. 94.)

*Preparation.* 1. Dry chlorine gas passed through pure bitter almond oil, is absorbed, with great rise of temperature and evolution of hydrochloric acid. The liquid must be ultimately heated to the boiling point, till the chlorine, on passing through, no longer generates hydrochloric acid. As soon as the evolution of hydrochloric acid slackens, the liquid acquires a yellow colour from the presence of dissolved chlorine, which however is given off on boiling. (Wöhler & Liebig.) — 2. When dry benzoic acid is heated to 100° with pentachloride of phosphorus, a violent action takes place, hydrochloric acid is evolved in large quantity, and a mixture of oxychloride of phosphorus and chloride of benzoyl passes over, from which between 198° and 200°, the chloride of benzoyl distils off, and may be purified from admixed pentachloride and oxychloride of phosphorus by treatment with a small quantity of water. (Cahours.) — 3. Oxychloride of phosphorus acts very violently on benzoate of soda at ordinary temperatures; and if to 1 pt. (1 At.) of the oxychloride there be taken not more than 2·81 pts. (3 At.) of benzoate of soda, the only products obtained are phosphate of soda and chloride of benzoyl:

$$3C^{14}H^5NaO^4 + PCl^3O^2 = 3C^{14}H^5ClO^2 + 3NaO,PO^5.$$

With a large proportion of benzoate of soda, anhydrous benzoic acid is formed at the same time. (Gerhardt.)

*Properties.* Transparent, colourless liquid, having a peculiar and extremely penetrating odour, attacking the eyes strongly, like horse-radish. Sp. gr. 1·196 (Wöhler & Liebig), 1·250 (Cahours). Boils at 195° (Malaguti), at 196° (Cahours). Vapour-density, 4·987 (Cahours).

| | | | Wöhler & Liebig. | Malaguti. | Cahours. |
|---|---|---|---|---|---|
| 14 C | 84·0 | 59·82 | 60·58 | 59·02 | 59·52 |
| 5 H | 5·0 | 3·56 | 3·74 | 3·67 | 3·52 |
| Cl | 35·4 | 25·21 | 24·42 | 24·73 | 25·02 |
| 2 O | 16·0 | 11·41 | 11·26 | 12·58 | 11·94 |
| $C^{14}ClH^5O^2$ | 140·4 | 100·00 | 100·00 | 100·00 | 100·00 |

| | Vol. | Density. |
|---|---|---|
| C-vapour | 14 | 5·8240 |
| H-gas | 5 | 0·3465 |
| Cl-gas | 1 | 2·4543 |
| O-gas | 1 | 1·1093 |
| Vapour of Chloride of Benzoyl | 2 | 9·7341 |
| | 1 | 4·8670 |

*Decompositions.* 1. Chloride of benzoyl burns with a bright, green-edged, very sooty flame. — 2. It decomposes slowly with cold water, quickly and completely with boiling water, into hydrochloric and benzoic acids. Similarly by long standing in contact with damp air. — 3. Heated with aqueous solutions of the alkalis, it forms a hydrochlorate and a benzoate. — 4. With dry ammoniacal gas it forms sal-ammoniac and benzamide; with aqueous ammonia, it forms sal-ammoniac and benzoate of ammonia. — 5. It may be distilled without alteration over anhydrous baryta or lime. — 6. With pentachloride of phosphorus it becomes strongly heated, terchloride of phosphorus being formed, together with a very strong smelling oily body not yet further examined. (Wöhler & Liebig.)

7. With metallic sulphides, iodides, bromides, or cyanides, it forms sulphide, iodide, bromide or cyanide of benzoyl. (Wöhler & Liebig.) — Heated with bichloride of tin in a sealed tube to 140°—200°, it is decomposed, yielding a small quantity of a black precipitate. The chlorides of magnesium, copper and zinc do not appear to act upon it. (Casselmann, *Ann. Pharm.* 98, 213.) — With sulphocyanide of potassium it becomes strongly heated and yields bisulphide of carbon and benzonitrite. (Schiff, *Ann. Pharm.* 99, 117.) According to Limpricht, sulphocyanide of benzoyl is first formed, and afterwards decomposes in the manner represented by the equation:

$$\underbrace{C^{14}H^5O^2,C^2NS^2}_{\text{sulphocyanide of benzoyl.}} = \underbrace{C^{14}NH^5}_{\text{benzonitrile.}} + CO^2 + CS^2.$$

8. With hydride of copper, chloride of benzoyl forms bitter almond oil and dichloride of copper. (Chiozza, *Compt. rend.* 26, 632):

$$Cu^2H + C^{14}ClH^5O^2 = C^{14}H^6O^2 + Cu^2Cl.$$

9. When it is mixed with dry and pulverised formiate of soda, a slight evolution of heat takes place, and on applying a gentle external heat, pure carbonic oxide gas is rapidly evolved, while benzoic acid sublimes and a residue is left consisting of benzoic acid and chloride of sodium:

$$C^2HNaO^4 + C^{14}ClH^5O^2 = C^{14}H^6O^4 + NaCl + 2CO.$$

The residue smells of formic acid set free by the action of the benzoic acid. (Gerhardt, *Ann. Pharm.* 87, 157.) — 10. When chloride of benzoyl is heated with the alkaline salts of the monobasic acids, metallic chlorides are formed, together with compounds of the anhydrous monobasic acid with anhydrous benzoic acid. (Gerhardt):

$$C^{14}ClH^5O^2 + C^4H^3NaO^4 = C^{14}H^5O^3,C^4H^3O^3 + NaCl.$$

11. Chloride of benzoyl heated with oxalate of potash forms anhydrous benzoic acid, chloride of potassium, carbonic oxide and carbonic acid. (Gerhardt, p. 94.) — 12. The solution of chloride of benzoyl in alcohol becomes heated in a few minutes to the boiling point, gives off hydrochloric acid, and when mixed with water, deposits oily drops of benzoate of ethyl.

¶ 13. When finely pulverised aldehyde-ammonia is added by very small portions to chloride of benzoyl, till the mass becomes solid, chloride of ammonium and benzoic acid are formed, together with a substance having, when dried at 100°, the composition $C^{32}N^2H^{16}O^4$ (isomeric or polymeric with hipparaffin, p. 82) The sal-ammoniac

may be extracted by water, the benzoic acid by solution of carbonate of soda, and if the residue be then digested in hot alcohol, a solution is obtained which yields the compound $C^{28}N^2H^{18}O^4$ in slender needles arranged in concentric groups. This substance melts when heated and sublimes partly undecomposed at a higher temperature. It is slowly decomposed by hot potash-ley, with formation of benzoic acid and separation of a brown resin; it is not altered by boiling with peroxide of lead and water; but on addition of sulphuric acid, aldehyde is given off and the liquid, if filtered hot, deposits crystals of benzamide; aldehyde and benzamide are likewise formed when the compound is stirred up with water and exposed to the action of nitrous acid. Sulphuric acid dissolves the compound when heated, forming a brown solution from which water separates a brown resin, and the liquid yields crystals of benzoic acid. The compound is insoluble in water; it dissolves sparingly in cold alcohol and ether; easily in the same liquids when heated. (Limpricht, *Ann. Pharm.* 99, 119.) T.

*Combinations.* Chloride of benzoyl, with the aid of heat, dissolves *sulphur* and *phosphorus*, which separate from it in the crystalline form on cooling. It mixes with *bisulphide of carbon* in all proportions and apparently without decomposition. (Wöhler & Liebig.) It dissolves *chloride of aluminium* with facility when heated, and the liquid solidifies in a crystalline mass on cooling. (Casselmann.)

*With Bichlorovinic Ether.* — $C^{18}Cl^3H^5O^3 = C^4Cl^2H^3O,C^{14}ClH^5O^2$. — Chlorine gas is passed at 60°—70° through benzoate of ethyl, whereupon hydrochloric acid and chloride of ethyl escape, and the liquid is distilled, after the action is complete, till the boiling point rises to 190°. The residue blackens even if the heat has not been raised to the boiling point. The distillate is shaken up with quicklime, redistilled at a temperature below its boiling point, as otherwise it blackens and gives off hydrochloric acid, and the liquid which passes over between 178° and 180°, is dried over quicklime in vacuo. (When chlorine gas is passed for a sufficient time through an alcoholic solution of benzoic acid, and the resulting oily liquid mixed with water, a yellowish oil is precipitated having an aromatic taste and smell. Bouillon-Lagrange, *J. Pharm.* 7, 200.)

Colourless liquid, of sp. gr. 1·346 at 10·8. Fumes slightly in the air, and has a suffocating odour like that of chloride of benzoyl. In dry air it does not redden litmus. Boils between 188° and 190°. The boiling point rises immediately in consequence of decomposition.

| | | | | Malaguti. |
|---|---|---|---|---|
| 18 C | 108·0 | 43·87 | | 43·34 |
| 5 H | 8·0 | 3·24 | | 3·44 |
| 3 Cl | 106·2 | 43·13 | | 42·50 |
| 3 O | 24·0 | 9·76 | | 10·72 |
| $C^{18}Cl^3H^5O^3$ | 246·2 | 100·00 | | 100·00 |

In contact with water, the compound is slowly resolved into benzoic, acetic and hydrochloric acids. (Malaguti, *Ann. Chim. Phys.* 70, 374; also *Ann. Pharm.* 32, 43; *J. pr. Chem.* 18, 56.)

*With Bitter almond oil.* — $C^{28}ClH^{11}O^4 = C^{14}H^6O^2,C^{14}ClH^5O^2$. — Formed in large quantity when crude bitter almond oil is imperfectly

decomposed by chlorine; sometimes also when bitter almond oil is decomposed by excess of chlorine. Colourless, shining laminæ resembling benzoic acid. Melts very easily and remains a long time fluid when at rest. Inodorous in the dry state.

| | | | Laurent & Gerhardt. |
|---|---|---|---|
| 28 C | 168·0 | 69·18 | 67·8 |
| 11 H | 11·0 | 4·46 | 4·6 |
| Cl | 35·4 | 14·37 | 14·0 |
| 4 O | 32·0 | 12·99 | 13·6 |
| $C^{28}H^{11}ClO^{4}$ | 246·4 | 100·00 | 100·0 |

Heated above its melting point, it gives off chloride of benzoyl. When moistened with water or alcohol, it gives off vapours of hydrochloric acid and emits an odour of bitter almond oil. Heated with water, it yields benzoic acid and bitter almond oil. Warm alcohol likewise decomposes it.

In cold alcohol the compound is sparingly soluble. (Laurent & Gerhardt, *Compt. chim.* 1850, 123.)

## Chlorobenzoic Acid.

$C^{14}ClH^{5}O^{4} = C^{14}ClH^{5},O^{4}$.

HERZOG. (1840) *N. Br. Arch.* 23, 15.
SCHARLING. *Ann. Pharm.* 41, 49; 42, 268.
STENHOUSE. *Ann. Pharm.* 55, 1; also *Phil. Mag. J.* 27, 179; also *J. pr. Chem.* 36, 248.
E. KOPP. *Compt. rend.* 24, 614; also *N. J. Pharm.* 11, 426; also *J. pr. Chem.* 41, 425.
FIELD. *Ann. Pharm.* 65, 55.
CHIOZZA. *N. Ann. Chim. Phys.* 36, 102; abstr. *Compt. rend.* 83, 317; *J. pr. Chem.* 57, 28.
LIMPRICHT & v. USLAR. *Ann. Pharm.* 102, 259.

*Chlorbenzoesäure, Acide benzoique monochloré, Chloromichmylsäure.*

*Formation.* 1. By the action of chlorine on benzoic acid. (Herzog.) According to Pisani (*N. Ann. Chim. Phys.* 45, 401), the so-called chloroniccic acid ($C^{12}ClH^{5}O^{4}$) which St.-Evre obtained by the action of chlorine on a solution of benzoic acid in excess of potash, (xi, 176), is nothing but chlorobenzoic acid contaminated with benzoic acid. — 2. By heating salicylic acid with pentachloride of phosphorus. (Chiozza.) — 3. By the action of chlorine on a heated mixture of cinnammic acid and strong soda-ley (E. Kopp), or by heating cinnamic acid with aqueous solution of chloride of lime, or with hydrochloric acid and chlorate of potash. (Stenhouse.) — 4. By the action of water on chloride of chlorobenzoyl (p. 117). (Limpricht & v. Uslar.)

*Preparation.* 1. When chlorine gas is passed over dry benzoic acid exposed to the sun, the acid is converted, in 12—48 hours, into a moist, viscid, gummy, somewhat reddish mass, which dissolves in carbonate of potash, with the exception of a brown-red substance which becomes resinous on exposure to the air. The brown-red solution is boiled with animal charcoal; the filtrate mixed with dilute nitric acid; and the resulting

precipitate washed with water till the wash-water no longer forms a cloud with nitrate of silver. (Herzog.) — 3. A mixture of salicylic acid and pentachloride of phosphorus melts with evolution of heat; on distilling the fluid mixture, the boiling point rises very rapidly, while hydrochloric acid is continually evolved, and a light deposit is formed in the neck of the retort; at length the mass blackens, swells up, and leaves a very light charcoal. On rectifying the distillate, the liquid which passes over between 200° and 250°, is a heavy, strongly refracting oil, which has a suffocating odour and is converted, gradually by cold and immediately by boiling water, into hydrochloric and chlorobenzoic acids. The heavy oil appears to be a compound of chlorobenzoic acid with hydrochloric acid, produced simultaneously with oxychloride of phosphorus. (Chiozza.)

$$C^{14}H^5O^4 + PCl^5 = C^{14}H^5ClO^4,ClH + PO^2Cl^3.$$

3. Urine [concentrated by evaporation? Gm.] is mixed with nitric acid; the liquid filtered from nitrate of urea; and the filtrate distilled. An acid liquid then passes over, together with a greenish yellow oil (nitrochloromichmyl), and a mass resembling benzoic acid is ultimately deposited in the neck of the retort. A larger quantity of this substance is obtained by neutralising the liquid, after the oil has been separated, with carbonate of soda or caustic ammonia, evaporating to dryness, and distilling the residue with dilute sulphuric acid (2 or 3 pts. of water to 1 pt. of oil of vitriol). The product is purified by washing with cold water and recrystallisation from hot water. (Scharling.) [The acid thus prepared is called by Scharling, *chloromichmylic acid;* but according to his own statements, it does not differ in any respect from chlorobenzoic acid. L.]

¶ 4. Chloride of chlorobenzoyl is boiled with potash; the alkaline solution precipitated with hydrochloric acid; and the precipitated chlorobenzoic acid dissolved in hot water: it then separates in small yellow needles which cannot be decolorised by recrystallisation and treatment with animal charcoal, but may be obtained perfectly white by combination with an alkali and reprecipitation by an acid. (Limpricht & v. Uslar.) ¶.

*Properties.* Colourless, inodorous, shining needles very much like salicylic acid. (Chiozza.) Crystallises from the alcoholic solution like benzoic acid (Herzog); in small concentrically grouped prisms, which never resemble the crystals of salicylic acid. (Limpricht & v. Uslar.) Melts at a temperature a few degrees above the melting point of benzoic acid (Chiozza); at 98° (Herzog); at about 140°, but sublimes at a lower temperature in small needles. (Limpricht & v. Uslar.) May be sublimed without decomposition.

| | | | Field. | Chiozza (2). | Scharling (3). | Limpricht & v. Uslar (4). |
|---|---|---|---|---|---|---|
| 14 C | 84·0 | 53·71 | 53·22 | 54·10 | 53·20 | 53·5 |
| 5 H | 5·0 | 3·20 | 3·22 | 3·23 | 3·36 | 3·2 |
| Cl | 35·4 | 22·63 | | 23·33 | 22·53 | 22·9 |
| 4 O | 32·0 | 20·46 | | 19·34 | 20·91 | 20·4 |
| $C^{14}H^5ClO^4$ | 156·4 | 100·00 | | 100·00 | 100·00 | 100·0 |

*Decompositions.* 1. Chlorobenzoic acid is converted by fuming nitric acid into nitrochlorobenzoic acid $C^{14}H^4ClXO^4$. (Limpricht & v. Uslar.)

— 2. With pentachloride of phosphorus, it yields chloride of chlorobenzoyl and chlorophosphoric acid. (Limpricht & v. Uslar.)

$$C^{14}H^5ClO^4 + PCl^5 = C^{14}H^4ClO^2,Cl + PO^2Cl^3 + HCl.$$

*Combinations.* Chlorobenzoic acid dissolves sparingly in cold, abundantly in boiling water.

The *Ammonia-salt* of the acid prepared by boiling benzoic acid with chlorate of potash and hydrochloric acid, does not melt easily, but blackens and deposits charcoal when heated. (Field.) The solution of chlorobenzoic acid (4) in ammonia gives off a large quantity of ammonia when evaporated over the water-bath, so that the residue consists of nearly pure chlorobenzoic acid. (Limpricht & v. Uslar.)

The *potash* and *soda-salts* cannot be obtained in crystals, but remain in gummy masses when their solutions are evaporated. (Limpricht & v. Uslar.)

*Chlorobenzoate of Baryta.* — Very soluble in water. The hot saturated solution of the salt prepared with the acid (2) solidifies on cooling in a crystalline radiated mass, or yields small dazzling white crystalline nodules. After drying over oil of vitriol, it does not give off any water at 100°. (Chiozza.) — The salt prepared with the acid (4) forms small needle-shaped crystals which give off 10·2 p. c. (3 At.) water at 100°. (Limpricht & v. Uslar.)

| | *At* 100°. | | | Chiozza. | Limpricht & v. Uslar. |
|---|---|---|---|---|---|
| $C^{14}ClH^4O^4$ | 155·4 | 69·38 | | | |
| Ba | 68·6 | 30·62 | | 30·49 | 30·25 |
| $C^{14}ClH^4BaO^4$ | 224·0 | 100·00 | | | |

*Chlorobenzoate of Lead.* — Small scaly crystals easily soluble in water; they give off 13·2 p. c. (3 At.) water at 100°. (Limpricht & v. Uslar.)

| | *At* 100°. | | Limpricht & v. Uslar. |
|---|---|---|---|
| $C^{14}ClH^4O^4$ | 155·4 | 88·7 | |
| Ca | 20·0 | 11·3 | 11·5 |
| $C^{14}ClH^4CaO^4$ | 175·4 | 100·0 | |

*Chlorobenzoate of Lead.* — White precipitate, which, after drying over oil of vitriol, does not suffer any further loss of weight at 110°, but melts and turns yellow. (Limpricht & v. Uslar.)

*Chlorobenzoate of Copper.* — Green precipitate.

*Chlorobenzoate of Silver.* — When a boiling solution of the ammonia-salt is mixed with nitrate of silver, small heavy crystals are deposited, and, as the liquid cools, larger crystals separate out. (Chiozza.) — White precipitate consisting of microscopic needles. (Limpricht & v. Uslar.)

| | *Dried over oil of vitriol.* | | | Chiozza. | Limpricht & v. Uslar. |
|---|---|---|---|---|---|
| 14 C | 84·0 | .... | 31·89 | 32·78 | |
| 4 H | 4·0 | .... | 1·52 | 1·54 | |
| Ag | 108·0 | .... | 41·04 | 40· 6 | 41·2 |
| Cl | 35·4 | .... | 13·44 | | |
| 4 O | 32·0 | .... | 12·11 | | |
| $C^{14}ClH^4AgO^4$ | 263·4 | .... | 100·00 | | |

Chlorobenzoic acid dissolves readily in *alcohol* and *ether*, and the alcoholic solution effloresces readily. (Herzog.) It dissolves in alcohol and ether and crystallises from the alcoholic solution in small concentrically grouped prisms. (Limpricht & v. Uslar.)

According to Stenhouse, when cinnamic acid is boiled with a saturated solution of chloride of lime as long as any oil passes over with the watery vapours, and the liquid filtered from the resulting carbonate of lime and compound of lime with resin, is treated with hydrochloric acid to expel the free chlorine, a crystalline acid is obtained on cooling, which, in different preparations, is sometimes chlorobenzoic acid, sometimes a mixture of chlorobenzoic acid with benzoic, bichlorobenzoic and terchlorobenzoic acids, which cannot be separated by crystallisation. The same products are obtained, according to Stenhouse, when benzoic acid is boiled with chloride of lime or with a mixture of hydrochloric acid and chlorate of potash.

## ¶. Chlorobenzoate of Ethyl.

$C^{18}H^9ClO^4 = C^4H^5O,C^{14}H^4ClO^3$.

LIMPRICHT & V. USLAR. *Ann. Pharm.* 102, 262.

Obtained by heating chloride of chlorobenzoyl (p. 116) with alcohol, or chlorobenzoic acid with alcohol and sulphuric acid, mixing the liquid with water, washing the precipitated ether with water, then drying it over chloride of calcium and rectifying.

Liquid smelling like benzoate of ethyl. Boils at 245°.

| | | | | Limpricht & v. Uslar. |
|---|---|---|---|---|
| 18 C | 108·0 | .... | 58·57 | |
| 9 H | 9·0 | .... | 4·88 | |
| Cl | 35·4 | .... | 19·20 | 19·1 |
| 4 O | 32·0 | .... | 17·35 | |
| $C^{18}H^9ClO^4$ | 184·4 | .... | 100·00 | |

The ether dissolves in a mixture of 2 pts. of oil of vitriol and 1 pt. fuming nitric acid; and if the liquid, after standing for 24 hours, be diluted with water, an oil is separated, which after a while yields crystals doubtless consisting of *nitrochlorobenzoate of ethyl;* from an alcoholic solution this compound separates in large colourless crystals. (Limpricht & v. Uslar.) ¶.

*Appendix to Chlorobenzoic Acid.*

## Nitrochloromichmyl.

SCHARLING. *Ann. Pharm.* 41, 49; 42, 269.

The greenish yellow oil which distils over in the preparation of chloromichmylic acid (chlorobenzoic acid p. 113) from the mother-liquor of nitrate of urea. It has a pungent odour and excites tears. Sp. gr. somewhat above 1·5.

It contains twice as much chlorine as chlorobenzoic acid, and is therefore probably $C^{14}H^4Cl^2O^2,NO^5$. [It is perhaps bichloronitrobenzoyl = $C^{14}Cl^2XH^3,O^2$, which would contain 38·22 p. c. C and 32·21 p. c. Cl, corresponding to the ratio 1 : 0·843; the ratio of the carbon to the chlorine in chlorobenzoic acid is 1 : 0·421 L.]

When boiled with water, it gradually forms chlorobenzoic and hydrochloric acids.—Treated with strong bases, it forms orange-coloured salts containing nitric acid and a peculiar colouring matter.—By cold oil of vitriol it is partially decomposed, a solid body being left which contains more or less chlorobenzoic acid. When distilled with oil of vitriol or treated with dilute carbonate of potash or soda, it yields *chloromichmyl*.—Dissolves readily in alcohol, with formation of nitrous ether.

## Chloromichmyl.

SCHARLING. *Ann. Pharm.* 42, 269.

*Formation* (vid. sup.).—Oil very sparingly soluble in water, readily in alcohol. It is slowly decomposed by caustic alkalis and alkaline carbonates. Resolved by heat into hydrochloric acid and chloromichmyl-resin.

*Chloromichmyl-resin* is also found in the residue of the distillation of the mother-liquor of nitrate of urea (p. 113), and may be purified by proper treatment with alcohol and ether. It is a mixture of several substances. Distilled with aqua-regia, it yields chloromichmylic acid and nitrochloromichmyl.

¶ *Chlorine-nucleus* $C^{14}H^4Cl^2$.

## Chloride of Chlorobenzoyl.

$$C^{14}H^4Cl^2O^2 = C^{14}H^4Cl^2,O^2\ [= C^{14}H^4ClO^2,Cl].$$

LIMPRICHT & V. USLAR. *Ann. Pharm.* 102, 262.

*Oxide of Bichlorobenzylene.*

*Preparation.* 1. By the action of pentachloride of phosphorus on chlorobenzoic acid:

$$\left.\begin{matrix}C^{14}H^4ClO^2\\H\end{matrix}\right\}O^2 + PCl^3,Cl^2 = C^{14}H^4ClO^2,Cl + HCl + PCl^3O^2.$$

2. By the decomposition of chlorosulphobenzoic acid:

$$C^{14}H^4Cl^2S^2O^6 = C^{14}H^4Cl^2O^2 + 2SO^2.$$

1 At. sulphobenzoic acid (p. 54) is heated in a retort with 2 At. pentachloride of phosphorus, as long as volatile products of distillation pass over; chlorosulphobenzoic acid is then formed and subsequently decom-

posed in the manner shown by the preceding equation. The distillate is rectified, and by repeated distillation a yellowish liquid is obtained which boils at 285°, and consists mainly of chloride of chlorobenzoyl, but is contaminated with other products which cannot be removed by distillation.

*Properties.* The chloride obtained by (1) is a transparent, colourless, strongly refracting liquid, boiling at 225°.

| | | | | Limpricht & v. Uslar (1). |
|---|---|---|---|---|
| 14 C | 84·0 | 48·0 | | |
| 4 H | 4·0 | 2·3 | | |
| 2 Cl | 70·8 | 40·5 | | 40·4 |
| 2 O | 16·0 | 9·2 | | |
| $C^{14}H^4ClO^2,Cl$ | 174·8 | 100·0 | | |

The product obtained by (2) contained about 34·5 p. c. chlorine and 1 p. c. sulphur.

*Decompositions.* 1. By boiling with water for several hours, the chloride is resolved into hydrochloric and chlorobenzoic acids. — 2. It is but slowly decomposed by dilute potash or ammonia; but strong aqueous ammonia converts it immediately into chlorobenzamide and sal-ammoniac.

$$C^{14}H^4ClO^2,Cl + 2NH^3 = C^{14}H^4ClO^2,NH^2 + NH^4Cl.$$

## Chlorosulphobenzoic Acid.

$$C^{14}H^4Cl^2S^2O^6 = C^{14}H^4Cl^2,2SO^3\ [= C^{14}H^4(S^2O^4)O^2,Cl^2].$$

LIMPRICHT & V. USLAR. *Ann. Pharm.* 102, 250.

*Sulphate of Bichlorobenzylene, Chloride of Sulphobenzoyl.*

*Preparation.* By the action of pentachloride of phosphorus on sulphobenzoic acid, water and chlorophosphoric acid being formed at the same time;

$$C^{14}H^4(S^2O^4)O^2\left.\begin{matrix}\\H^2\end{matrix}\right\}O^4 + PCl^5,Cl^2 = C^{14}H^4(S^2O^4)O^2,Cl^2 + PCl^3O^2 + 2HO.$$

1 pt. (1 At.) of perfectly dry and pulverised sulphobenzoic acid is gently heated in a turbulated retort with 2 pts. (rather more than 2 At.) of pentachloride of phosphorus; the mixture heated after the action has ceased, first over the water-bath, and then to 170° to remove the chlorophosphoric acid; and the residue rapeatedly washed with water, which removes the last portions of chlorophosphoric acid but exerts only a very slight action on the chlorobenzoic acid. The adhering water is removed as completely as possible by means of bibulous paper, and the last portions by standing over oil of vitriol.

*Properties.* Yellowish brown, viscid oil which cannot be distilled without decomposition. The colour is due to impurity. It is heavier than water and has a faint but unpleasant odour.

| | | | Limpricht & v. Uslar. |
|---|---|---|---|
| 14 C | 84·0 | 35·1 | 37·3 |
| 4 H | 4·0 | 1·6 | 2·4 |
| 2 Cl | 70·8 | 29·8 | 28·2 |
| 2 S | 32·0 | 13·4 | 13·7 |
| 6 O | 48·0 | 20·1 | 18·4 |
| $C^{14}H^4Cl^2S^2O^6$ | 238·8 | 100·0 | 100·0 |

The difference between the analytical and calculated results doubtless arises from decomposition taking place during the preparation.

Limpricht & v. Uslar regard the compound as the chloride of the biatomic radical sulphobenzoyl $C^{14}H^4(S^2O^4)O^2$, formed from benzoyl $C^{14}H^5O^2$ by the substitution of $S^2O^4$, for 1 At. hydrogen, sulphobenzoic acid being $\left.\begin{matrix}C^{14}H^4(S^2O^4)O^2\\H^2\end{matrix}\right\}O^2$, and chlorosulphobenzoic acid $\left.\begin{matrix}C^{14}H^4(S^2O^4)O^2\\Cl^2\end{matrix}\right\}$.

*Decompositions.* 1. The acid is decomposed by *distillation.* At temperatures above 300° it boils violently, giving off sulphurous acid, yielding a distillate of chloride of chlorobenzoyl (p. 116), and leaving a residue of charcoal. — 2. It is slowly decomposed by *water* at ordinary temperatures, and when heated with water to 100° in a sealed tube, it disappears in a few hours, being converted into hydrochloric and sulphobenzoic acids:

$$C^{14}H^4Cl^2S^2O^6 + 4HO = 2HCl + C^{14}H^6S^2O^{10}.$$

3. The *fixed alkalis* decompose it, forming an alkaline chloride and a sulphobenzoate. — 4. Gaseous *ammonia* exerts scarcely any action upon it, and dry carbonate of ammonia decomposes it but slightly; but concentrated aqueous ammonia dissolves it readily, forming sal-ammoniac and sulphobenzamide:

$$C^{14}H^4(S^2O^4)O^2,Cl^2 + 2NH^3 = C^{14}H^4(S^2O^4)O^2,NH^2 + NH^4Cl.$$

Alcohol saturated with ammonia dissolves it, forming ethylosulphobenzoate of ammonia. When ammoniacal gas is passed through a solution of the compound in ether, sulphobenzamide is formed, together with various other products. — 5. *Aniline* in contact with it becomes strongly heated, yielding sal-ammoniac and sulphobenzanilide.

Chlorosulphobenzoic acid is insoluble in water. Alcohol dissolves it, but with great rise of temperature and decomposition, forming sulphobenzoate of ethyl. In *ether* it appears to dissolve without decomposition. ¶.

*Cyanogen-nucleus* $C^{14}CyH^5$.

## Cyanide of Benzoyl.

$C^{16}NH^5O^2 = C^{14}CyH^5,O^2$.

WÖHLER & LIEBIG. *Ann. Pharm.* 3, 267; also *Pogg.* 26, 342.
KOLBE. *Ann. Pharm.* 90, 62.

*Formation and Preparation.* When chloride of benzoyl is distilled with cyanide of mercury, a golden yellow oil is obtained, which may be rendered colourless by rectification (Whöler & Liebig), and after a while

solidifies in a crystalline mass, which must be washed with warm water, till the wash-water is no longer blackened by sulphuretted hydrogen, then pressed between bibulous paper, and dried over oil of vitriol, (Kolbe.)

*Properties.* Crystallises by slow cooling in tables an inch long, melts at 31°, and often does not solidify on cooling till after it has been agitated. Boils between 206° and 208°. (Kolbe.) Has a pungent odour and excites tears.

| | | | Kolbe. |
|---|---|---|---|
| 16 C | 96 | 73·28 | 73·3 |
| N | 14 | 10·68 | |
| 5 H | 5 | 3·82 | 3·9 |
| 2 O | 16 | 12·22 | |
| $C^{16}NH^5O^2$ | 131 | 100·00 | |

Very inflammable; burns with a white very sooty flame. With dry ammoniacal gas it forms hydrocyanate of ammonia and benzamide. (Wöhler & Liebig.)

*Nitro-nucleus* $C^{14}XH^5$.

## Nitrobenzaldide.

$C^{14}NH^5O^6 = C^{14}XH^5,O^2$.

BERTAGNINI. *N. Ann. Chim. Phys* 33, 465; also *Ann. Pharm.* 79, 259; abstr. *Compt. rend.* 32, 688. — Further *Ann. Pharm.* 86, 190.

*Hydride of Nitrobenzoyl, Nitrobenzoylwasserstoff, Nitrobittermandelöl.*

*Formation and Preparation.* When bitter almond oil is gradually added to fuming nitric acid kept cool by external refrigeration, or to 15 or 20 times its volume of a cold mixture of 1 vol. nitric acid of sp. gr. 1·32 and 2 vol. oil of vitriol, and the resulting solution, whose formation is attended with rise of temperature, is mixed with water after standing for half an hour or an hour, yellowish drops separate out, which crystallise after a few days. At the same time, a yellow oily substance is produced having a strong and somewhat alliaceous odour. — If the liquid is not sufficiently cooled during the preparation, nitrobenzoic acid is likewise formed. — The crystalline mass, after being washed in linen with cold water, and pressed between two porous tiles till the residue is no longer yellow, and no longer renders the paper greasy between which it is pressed, is dissolved in a small quantity of boiling alcohol, which on cooling deposits the compound, partly in crystals, partly in the form of an oil which crystallises after a while: both portions of the product are recrystallised from alcohol mixed with water (or from hot water, which however dissolves a small quantity).

*Properties.* White shining needle-shaped crystals. After fusion it begins to crystallise at 46°, on agitating the melted mass, the thermometer immediately rises to 49°. May be evaporated in small quantities without decomposition. Emits a very faint odour at ordinary tempera-

tures; but a very agreeable odour when heated somewhat above its melting point; when evaporated in considerable quantities, it emits very pungent vapours. Has a pungent taste, somewhat resembling that of bitter almond oil.

| | | | | Bertagnini. |
|---|---|---|---|---|
| 14 C | 84 | 55·62 | | 55·76 |
| N | 14 | 9·27 | | 9·42 |
| 5 H | 5 | 3·31 | | 3·49 |
| 6 O | 48 | 31·80 | | 31·33 |
| $C^{14}NH^5O^6$ | 151 | 100·00 | | 100·00 |

*Decompositions.* 1. Nitrobenzaldide remains unaltered in the air even when warm. It burns with a sooty flame. — 2. Heated with an oily mixture of *nitric acid* and *oil of vitriol*, it yields nitrobenzoic acid. — 3. In concentrated *chromic acid*, it dissolves quickly, with rise of temperature, and solidifies into a crystalline mass of nitrobenzoic acid. — 4. *Chlorine* does not act upon nitrobenzaldide in ordinary daylight, but in sunshine it forms chloronitrobenzoyl. — *Bromine* dissolves readily in fused nitrobenzaldide, but does not decompose it till heated above 100°. — 5. It dissolves readily in aqueous *potash;* the solution remains unaltered at ordinary temperatures; but on the application of heat, nitrobenzoate of potash is quickly produced; the solution in alcoholic potash solidifies very quickly at ordinary temperatures into a transparent jelly of nitrobenzoate of potash, in which small nodular crystals of this salt make their appearance. [After nitrobenzaldide has been heated with alcoholic potash, the addition of water throws down a brown viscid resin, while nitrobenzoate of potash remains in solution. (List & Limpricht.)] — 6. Aqueous or alcoholic *ammonia* converts nitrobenzaldide into ternitrohydrobenzamide $C^{42}X^3N^2H^{15}$, which may change into ternitroamarine by simple metamorphosis. — The same transformation takes place in ammoniacal gas, a large quantity of water being given off at the same time:

$$3C^{14}XH^5O^2 + 2NH^3 = C^{42}X^3N^2H^{15} + 6HO.$$

7. The alcoholic solution of nitrobenzaldide yields, when *sulphuretted hydrogen* is passed through it, a precipitate of sulphide of nitrobenzylene $C^{14}XH^5S^2$. — 8. When *sulphuretted hydrogen* is passed through the solution of nitrobenzaldide in *alcoholic ammonia* and the liquid heated from time to time, a semifluid substance is deposited mixed with a large quantity of sulphur. When this substance is extracted with ether, after decanting the alcoholic liquid, an ethereal solution is obtained, which leaves on evaporation a reddish, very viscid mass, insoluble in water or hydrochloric acid, but dissolving with tolerable facility in warm alcohol; when heated, it swells up, gives off sulphuretted hydrogen, and burns with a bright flame, leaving a slowly combustible charcoal. Nitrobenzaldide boiled with nitric acid yields sulphuric acid and a yellow resin. — 9. Heated with *sulphite* of ammonia, it yields a body which is soluble in water and appears to be an acid. — 10. Strong *hydrocyanic* acid dissolves nitrobenzaldide with facility. If the solution is evaporated immediately, the nitrobenzaldide separates unaltered; but after standing for a few hours, the solution yields on evaporation a viscid liquid permanent in the air, which when dissolved in hot water, separates in drops on

cooling, and when boiled with hydrochloric acid, yields sal-ammoniac and another body soluble in water. — Cyanide of potassium quickly converts nitrobenzaldide into a peculiar substance. — 11. When urea is thrown into melted nitrobenzaldide and the liquid gently heated, water escapes, and the whole solidifies on cooling into an opaque mass, which dissolves sparingly in pure alcohol, but readily in alcohol mixed with hydrochloric acid; urea and nitrobenzaldide being then reproduced.

*Combinations.* 1. Nitrobenzaldide dissolves sparingly in cold water, but with tolerable facility in boiling *water;* the solution saturated at the boiling heat becomes milky on cooling, and afterwards filled with shining needles. — 2. It dissolves without decomposition in *oil of vitriol, hydrochloric acid* and *nitric acid;* from the solution in oil of vitriol, it separates in shining laminæ as the liquid absorbs water from the air.

3. With *Bisulphite of Ammonia.* — $C^{14}XH^5O^2 + NH^4O,2SO^2 + 2Aq$. — Easily obtained by treating nitrobenzaldide with an aqueous solution of bisulphite of ammonia of 29° B. or by mixing it with aqueous ammonia and passing sulphurous acid gas through the liquid. On applying a gentle heat, the nitrobenzaldide dissolves very abundantly in the bisulphite of ammonia; (at a higher temperature, the sulphurous acid exerts a decomposing action;) on cooling the compound crystallises out. — It crystallises from alcohol in small, colourless, transparent prisms, which grate between the teeth, and have a bitter and sulphurous taste.

| | | | Bertagnini. |
|---|---|---|---|
| 14 C | 84 | 32·43 | 32·79 |
| 2 N | 28 | 10·81 | 11·12 |
| 11 H | 11 | 4·24 | 4·40 |
| 2 S | 32 | 12·35 | |
| 13 O | 104 | 40·17 | |
| $C^4NH^5O^6 + NH^4O,2SO^2 + 2Aq$ | 259 | 100·00 | |

The compound is not altered by exposure to the air, though the crystals sometimes assume a faint violet tinge. — The aqueous solution is decomposed by boiling, nitrobenzaldide being set free. Acids do not alter the solution at ordinary temperatures, but on heating the liquid, decomposition takes place, attended with evolution of sulphurous acid. The compound gives off ammonia when heated with alkalis. The aqueous solution forms with barium, lead, and silver salts, white precipitates consisting of the sulphites of those metals, and after a while crystals of the nitro-compound make their appearance; with chloride of platinum, chloroplatinate of ammonia is produced.

The compound dissolves readily in *water*, and crystallises with difficulty from the solution. Nitrobenzaldide dissolves very easily in water containing bisulphite of ammonia. — The compound dissolves with facility in boiling *alcohol.*

4. *With Bisulphite of Soda.* — $C^{14}XH^5O^2 + NaO,HO,2SO^2 + 10Aq$. — When nitrobenzaldide is dissolved at a gentle heat in aqueous bisulphite of soda of about 27° B., the liquid yields on cooling, shining yellow laminæ, which are rendered colourless by recrystallisation from hot water, effloresce in the air, and give off 26·08 p.c. (10 At.) water at 90°.

| | *At* 90°. | | | Bertagnini. |
|---|---|---|---|---|
| 14 C | 84 | .... | 32·94 | 32·69 |
| N | 14 | .... | 5·49 | |
| 6 H | 6 | .... | 2·35 | 2·53 |
| 2 S | 32 | .... | 12·54 | |
| NaO | 31 | .... | 12·15 | 12·34 |
| 11 O | 88 | .... | 34·53 | |
| $C^{14}NH^5O^6 + NaO,HO,2SO^2$ | 255 | .... | 100·00 | |

The compound dissolves sparingly in cold, easily in boiling water; the solution decomposes quickly when boiled, giving off the odour of nitrobenzaldide. Boiled with acids, it yields nitrobenzaldide and sulphurous acid.

5. Nitrobenzaldide dissolves readily in *alcohol*, and with tolerable facility in *ether*.

## Nitrobenzoic Acid.

$C^{14}NH^5O^8 = C^{14}XH^5,O^4$.

PLANTAMOUR. (1839.) *Ann. Pharm.* 30, 349.
MULDER. *J. pr. Chem.* 18, 253; 19, 362; also *Ann. Pharm.* 34, 297.
MITSCHERLICH. *J. pr. Chem.* 22, 196.
MARCHAND. *J. pr. Chem.* 18, 254; 19, 365.
ABEL. *Ann. Pharm.* 63, 313; also *Mem. Chem. Soc.* 3, 445.
H. BLUMENAU. *Ann. Pharm.* 87, 127.
BERTAGNINI. *Ann. Pharm.* 79, 259.
GERLAND. *Ann. Pharm.* 91, 185.

*Nitrobenzoesäure, Nitrocinnolsäure, Nitrobenzinsäure, Benzoesalpetersäure, Acide nitrobenzique.*

*Formation.* 1. By the action of nitrosulphuric or chromic acid on nitrobenzaldide. — 2. By heating nitric acid with benzoic acid (Mulder, E. Kopp, *Compt. chim.* 1849, 149), with cinnamic acid (Plantamour, Mulder); by continued boiling of nitric acid with cumol (Abel); by boiling dragon's blood with dilute nitric acid (Blumenau) — 3. In the decomposition of hippuric acid by hydrochloric acid. (Bertagnini.) — 4. By the action of nitrosulphuric acid on benzoic acid or chloride of benzoyl; in the latter case, chlorine is evolved, together with another gas which excites a copious flow of tears. (Voit.)

*Preparation.* 1. Benzoic acid is boiled with excess of nitric acid, till the solution, which is red at first, becomes decolorised and gives off nitrous vapours; the nitrobenzoic acid crystallises out on cooling and may be purified by recrystallisation from hot water. (Mulder.) It is only necessary to heat for a short time in order to convert the whole of the benzoic acid into nitrobenzoic acid; the nitrous fumes arise from a further action of the nitrous acid on the nitrobenzoic acid. (Mitscherlich.) It is only by continued boiling with frequently renewed portions of nitric acid that benzoic acid can be completely converted into nitrobenzoic acid. (Gerland.) — 2. Oil of vitriol is added with agitation, to a mixture of 1 pt. of benzoic acid with 2 pts. of nitre, the mixture heated till

it softens, and the resulting nitrobenzoic acid purified by crystallisation from water. With small quantities, the mixture may be heated till it melts; if it be then left to cool quietly, the bisulphate of potash crystallises out first, and the nitrobenzoic acid decanted from it is perfectly pure after two crystallisations. (Gerland). Or, fused benzoic acid is added by small portions to a mixture of 2 pts. strong sulphuric acid and 1 pt. nitric acid of sp. gr. 1·5, and gently heated for about half an hour; on subsequently adding water to the liquid, nitrobenzoic acid is precipitated in white flakes. (Voit, *Ann. Pharm.* 99, 100.) — 3. When cumol is heated with fuming nitric acid for several hours, nitrobenzoic acid crystallises as the liquid cools, and may be freed from adhering binitrocumol by treating the solution with ammonia and precipitating with nitric acid. (Abel.) — 4. When dragon's blood is boiled with excess of nitric acid of sp. gr. 1·34 mixed with an equal quantity of water, it dissolves gradually with evolution of red vapours. When no more vapours escape, the liquid is evaporated to dryness; the cooled mass pressed between paper, and saturated with carbonate of soda; the solution purified with animal charcoal and precipitated by nitric acid; and the precipitate washed with cold water. The mass consisting of fine scales contains a substance which chars when heated, together with nitrobenzoic acid which sublimes. (Blumenau.)

*Properties.* Colourless, crystalline laminæ generally grouped together. In water it melts below 100°, forming an oil which solidifies on cooling in a hard, brittle crystalline mass; by itself it melts at 127°, and begins to sublime at 110°. The pure acid sublimes completely and without decomposition in slender needles; when coloured it leaves a small quantity of charcoal. The vapours have a pungent odour and excite coughing. The acid reddens litmus. (Mulder.)

| | | | Plantamour. | Mulder. | Marchand. | Abel. | Bertagnini. |
|---|---|---|---|---|---|---|---|
| 14 C | 84 | 50·73 | 50·14 | 50·42 | 50·19 | 50·30 | 50·30 |
| N | 14 | 8·39 | | 8·35 | 8·36 | 8·38 | 8·63 |
| 5 H | 5 | 2·96 | 3·06 | 3·02 | 2·99 | 3·00 | 3·12 |
| 8 O | 64 | 37·92 | | 38·21 | 38·46 | 38·32 | 37·95 |
| $C^{14}NH^5O^8$ | 167 | 100·00 | | 100·00 | 100·00 | 100·00 | 100·00 |

The acid analysed by Plantamour was prepared from cinnamic acid; that by Mulder, from benzoic acid; that by Marchand, from cinnamic acid; that by Abel, from dragon's blood; and that by Bertagnini from nitrohippuric acid.

*Decompositions.* 1. The acid when heated to its boiling point, blackens and gives off combustible gases. (Mulder.) — 2. It dissolves in strong *nitric acid*, without decomposition (Mulder); it is decomposed by continued boiling with nitric acid. (Mitscherlich.) — 3. It is not altered by sublimation in *chlorine gas.* (Mulder.) — 4. It dissolves without colour in *oil of vitriol;* on heating the solution, a small quantity of the acid sublimes without alteration, and near the boiling point of oil of vitriol, the liquid turns red without giving off gas; if a larger quantity of water be then added, a few grey flakes are separated, and the liquid on being saturated with carbonate of baryta, forms a solution containing a peculiar substance not yet further examined. (Mulder.) — 5. By *pentachloride of phosphorus,* the acid is not attacked at ordinary temperatures; but on the application of a gentle heat, a violent action takes

place, attended with formation of chloronitrobenzoyl and chlorophosphoric acid. (Bertagnini.)—6. With *hydrosulphate of ammonia* it forms benzamic acid (Zinin):

$$C^{14}NH^{5}O^{6} + 6HS = C^{14}NH^{7}O^{8} + 4HO + 6S.$$

7. When boiled with *sulphite of ammonia*, it behaves like nitronaphthalin. (Piria.)—8. Heated with excess of *lime*, it yields various products not containing nitrobenzol. (Mulder.)

*Combinations.* Nitrobenzoic acid dissolves in 400 pts. of water at 10°, and in 10 pts. of boiling water.

It is a strong acid and expels many other acids from their salts. The *nitrobenzoates* are for the most part soluble in water and alcohol, and detonate when heated.

*Nitrobenzoate of Ammonia.*—a. *Neutral.*—100 pts. of dry nitrobenzoic acid take up at ordinary temperatures 8·04 pts. of ammonia, corresponding to 1 At. ammonia with 1 At. acid. (Mulder.) [Calculation requires 10·17 pts. of ammonia to 100 pts. of acid. L.]—*b. Acid.*—Crystallises by evaporation from a solution of nitrobenzoic acid in ammonia in white somewhat shining needles. (Mulder.) According to Mulder, 100 pts. of the acid at 100° take up 3·72 pts. of ammoniacal gas, agreeing approximately with 1 At. ammonia to 2 At. acid [calculation requires 5·08 pts. L.].

| | | | | Mulder, *crystallised.* |
|---|---|---|---|---|
| 28 C | 168 | .... | 47·86 | ..... 47·22 |
| 3 N | 42 | .... | 11·97 | |
| 13 H | 13 | .... | 3·70 | ..... 4·11 |
| 16 O | 128 | .... | 36·47 | |
| $C^{14}XH^{4}(NH^{4})O^{4} + C^{14}XH^{5}O^{4}$ | 351 | .... | 100·00 | |

Heated on platinum foil it yields nitrobenzol. (Mulder.)

*Nitrobenzoate of Potash.*—The solution of the acid in potash yields on evaporation either small crystals or a soapy mass, according to its degree of concentration. When heated on platinum-foil, it melts, and splits up, with emission of sparks, into black vermiform masses three or four inches long. A large quantity of nitrobenzol is given off at the same time. (Mulder.)

*Nitrobenzoate of Soda.*—Prepared by dissolving the acid in caustic soda. Deliquescent and difficult to crystallise. Behaves like the potash-salt when heated. (Mulder.) Does not deliquesce in the air. (Mitscherlich.)

*Nitrobenzoate of Baryta.*—When the acid is boiled with water and excess of carbonate of baryta, the solution yields on cooling beautiful shining crystals, which give off 13·22 per cent. (4 At.) of water at 100°.

| *Crystallised.* | | | | Mulder. |
|---|---|---|---|---|
| $C^{14}NH^{4}O^{7}$ | 158·0 | .... | 58·38 | |
| BaO | 76·6 | .... | 28·31 | ..... 28·40 |
| 4 HO | 36·0 | .... | 13·31 | ..... 13·94 |
| $C^{14}NH^{4}BaO^{8} + 4Aq$ | 270·6 | .... | 100·00 | |

*Nitrobenzoate of Strontia.* — When the acid is boiled with water and carbonate of strontia, and the solution evaporated to the crystallising point, it yields on cooling feathery needles united in tufts and destitute of lustre. After drying in the air, it gives off 9·52 per cent. ($2\frac{1}{2}$ At.) water at 150°. (Mulder.)

| | | | | Mulder. |
|---|---|---|---|---|
| $2\,C^{14}NH^4O^7$ | 316 | .... | 67·96 | |
| $2\,SrO$ | 104 | .... | 22·36 | ..... 19·22 |
| $5\,HO$ | 45 | .... | 9·68 | ..... 9·52 |
| $2(C^{14}NH^4SrO^8) + 5Aq$ | 465 | .... | 100·00 | |

*Nitrobenzoate of Lime.* — When the acid is boiled with water and carbonate of lime and the solution evaporated, it yields on cooling, small white, faintly lustrous crystals, which give off 9·09 p. c. (2 At.) water between 130° and 190°. (Mulder.)

| *Crystallised.* | | | | Mulder. |
|---|---|---|---|---|
| $C^{14}NH^4O^7$ | 158 | .... | 77·45 | |
| $CaO$ | 28 | .... | 13·72 | ..... 14·00 |
| $2\,HO$ | 18 | .... | 8·83 | ..... 9·05 |
| $C^{14}NH^4CaO^8 + 2Aq$ | 204 | .... | 100·00 | |

When heated above 190°, it melts, blackens, gives off nitrobenzol, and finally detonates. (Mulder.)

*Nitrobenzoate of Manganese.* — A solution of the acid in ammonia mixed with sulphate of manganese yields by evaporation, white crystals containing 4 At. water, of which 2 At. (7·16 p. c.) go off between 40° and 70°, and the rest between 115° and 183°. At 115°, the salt begins to assume a yellow colour.

| *Crystallised.* | | | | Mulder. |
|---|---|---|---|---|
| $C^{14}NH^4O^7$ | 158·0 | .... | 69·03 | |
| $MnO$ | 35·6 | .... | 15·42 | ..... 16·23 |
| $4\,HO$ | 36·0 | .... | 15·55 | ..... 14·78 |
| $C^{14}NH^4MnO^8 + 4Aq$ | 229·6 | .... | 100·00 | |

*Nitrobenzoate of Zinc.* — *a. Quadribasic.* — Acid nitrobenzoate of ammonia added to a solution of sulphate of zinc, throws down a basic salt in the form of a gelatinous precipitate. (Mulder.)

| | | | | Mulder, at 130°. |
|---|---|---|---|---|
| $C^{14}NH^4O^7$ | 158·0 | .... | 47·92 | |
| $4\,ZnO$ | 160·8 | .... | 52·08 | ..... 51·8 |
| $3ZnO,C^{14}NH^4ZnO^8$ | 318·8 | .... | 100·00 | |

*b. Monobasic.* — The liquid filtered from *a* yields by evaporation, laminar crystals which give off 18·61 p. c. (5 At.) water at 140°. (Mulder.)

| | | | | Mulder. |
|---|---|---|---|---|
| $C^{14}NH^{4}O^{7}$ | 158·0 | 64·96 | | |
| ZnO | 40·2 | 16·53 | | 16·00 |
| 5 HO | 45·0 | 18·51 | | 18·61 |
| $C^{14}NH^{4}ZnO^{8}$ + 5Aq | 243·2 | 100·00 | | |

*Nitrobenzoate of Lead.* — *a. Basic.* — Obtained by carefully precipitating the aqueous acid with basic acetate of lead, or nitrobenzoate of potash with the neutral acetate, and drying the white precipitate at 100°.

| | | | Mulder (1). | Mulder (2). |
|---|---|---|---|---|
| 70 C | 420·0 | 28·75 | 28·96 | 29·13 |
| 5 N | 70·0 | 4·80 | | |
| 20 H | 20·0 | 1·36 | 1·57 | 1·42 |
| 6 PbO | 670·8 | 45·92 | 45·41 | 45·42 |
| 35 O | 280·0 | 19·17 | | |
| $PbO,5C^{14}NH^{4}PbO^{8}$ | 1460·8 | 100·00 | | |

The same salt remains undissolved when *b* is washed.

When nitrobenzoic acid is boiled with water and carbonate of lead, a large quantity of carbonic acid escapes, and two salts are produced, one of which is soluble while the other forms insoluble flakes. (Mulder.)

*b. Normal.* — When a boiling saturated aqueous solution of nitrobenzoic acid is mixed with basic acetate of lead, till a permanent precipitate is formed, the liquid on cooling, yields even at 90°, stellate crystals which soon fill the entire liquid, so that it solidifies into a white mass; this must be thrown on a filter and pressed. A less concentrated solution yields on cooling more distinct crystals, which, when once formed, are insoluble even in the boiling liquid. — The same salt is produced when a solution of *a* in acetic acid is dropped into a boiling solution of nitrobenzoic acid.

| | | | Mulder. |
|---|---|---|---|
| 14 C | 84·0 | 31·13 | 31·05 |
| N | 14·0 | 5·19 | |
| 4 H | 4·0 | 1·48 | 1·53 |
| PbO | 111·8 | 41·45 | 41·53 |
| 7 O | 56·0 | 20·75 | |
| $C^{14}NH^{4}PbO^{8}$ | 269·8 | 100·00 | |

*Ferric Nitrobenzoate.* — Obtained by precipitating a boiling solution of the acid with aqueous ferric chloride. Bulky flesh-coloured powder, insoluble even in boiling water. After drying in the air, it does not give off any water even at 135°. (Mulder.)

| | | | Mulder. |
|---|---|---|---|
| 3 $C^{14}NH^{4}O^{7}$ | 474 | 84·65 | |
| $Fe^{2}O^{3}$ | 80 | 15·35 | 15·23 |
| $Fe^{2}O^{3}$ $3C^{14}NH^{4}O^{7}$ | 554 | 100·00 | |

*Nitrobenzoate of Copper.* — When a hot solution of the acid is mixed with acetate of copper, the liquid on cooling deposits a blue powder which gives off water at 130°, and part of its acid at the same time.

| | | | Mulder. |
|---|---|---|---|
| $C^{14}NH^4O^7$ | 158·0 | 76·40 | |
| CuO | 39·8 | 19·24 | 18·96 |
| HO | 9·0 | 4·36 | 5·53 |
| $C^{14}NH^4CuO^8$ + Aq | 206·8 | 100·00 | |

*Nitrobenzoate of Silver.* — Obtained by precipitating an ammoniacal solution of the acid with nitrate of silver, and pressing the precipitate. It passes through the filter in washing. (Mulder.) The precipitate is crystallised from hot water, then washed and the crystals dried. (Abel.) It crystallises from the aqueous solution in laminæ having a pearly lustre (Mulder):

| | | | Mulder. | Plantamour. | Abel. | List & Limpricht. |
|---|---|---|---|---|---|---|
| 14 C | 84·0 | 30·65 | 30·69 | | | |
| N | 14·0 | 5·11 | 5·06 | | | |
| 4 H | 4·0 | 1·46 | 1·57 | | | |
| Ag | 108·1 | 39·42 | 38·86 | 40·37 | 39·24 | 39·34 |
| 8 O | 64·0 | 23·36 | 23·82 | | | |
| $C^{14}NH^4AgO^8$ | 274·1 | 100·00 | 100·00 | | | |

At 120°, part of the acid volatilises, the salt turns grey and continues to give off acid; at 250°, in close vessels the salt explodes, with formation of nitrobenzol and empyreumatic products. (Mulder.)

By dry distillation, the salt yields a large quantity of nitrobenzol. (Mulder, Abel.) Heated on platinum foil, it melts and burns without detonation. (Mulder.)

Nitrobenzoic acid dissolves in *alcohol* (Mulder) in less than 1 pt. of alcohol at 20°. (Mitscherlich; E. Kopp, *Compt. chim.* 1849, 149.) It dissolves readily in *ether*.

## Nitrobenzoate of Methyl.

$C^{16}NH^7O^8 = C^2H^3O,C^{14}XH^4O^3$.

CHANCEL. *Compt. chim.* 1849, 179; also *J. pr. Chem.* 47, 142; abstr. *Ann. Pharm.* 72, 274.
BERTAGNINI. *Ann. Pharm.* 79, 269; also *N. Ann. Chim. Phys.* 33, 473.

*Formation and Preparation.* 1. When hydrochloric acid gas is passed through a boiling solution of nitrobenzoic acid in wood-spirit, till part of the wood-spirit is distilled off, the residue consists of two layers, the lower of which is nitrobenzoate of methyl, while the upper is a solution of the same compound in wood-spirit, whence it may be precipitated by water. The whole of the compound ether thus produced is shaken up with a hot

solution of carbonate of soda, repeatedly washed with cold water, pressed between paper, and crystallised from alcohol or from a mixture of alcohol and ether. — 2. A solution of chloronitrobenzoyl in wood-spirit soon deposits crystals of nitrobenzoate of methyl. (Bertagnini.)

Small, white, nearly opaque, right rombic prisms, $u : u = 118°$ to $120°$, melts at 70°, boils at 279°. Has a very faint aromatic odour and a fresh taste.

| | | | | | Chancel. |
|---|---|---|---|---|---|
| 16 C | 96 | | 53·04 | | 52·92 |
| N | 14 | | 7·73 | | 7·87 |
| 7 H | 7 | | 3·86 | | 3·93 |
| 8 O | 64 | | 35·37 | | 35·28 |
| $C^{16}NH^{7}O^{8}$ | 181 | | 100·00 | | 100·00 |

Its reactions are exactly similar to those of nitrobenzoate of ethyl.

It is insoluble in water, sparingly soluble in *alcohol* and in *ether*, somewhat more in *wood-spirit*.

## Nitrobenzoate of Ethyl.

$C^{18}NH^{9}O^{8} = C^{4}H^{5}O,C^{14}XH^{4}O^{3}$.

MITSCHERLICH. *Lehrb.* 4 Aufl. 1, 221.
E. KOPP. *Compt. rend.* 34, 615; also *N. J. Pharm.* 11, 427.
CHANCEL. *Compt. chim.* 1849, 177; also *J. pr. Chem* 47, 140.
BERTAGNINI. *Ann. Pharm* 79, 269; also *N. Ann. Chim. Phys.* 33, 473.
LIST & LIMPRICHT. *Ann. Pharm.* 90, 206.

*Formation and Preparation.* 1. An alcoholic solution of nitrobenzoic acid is continuously boiled with a small quantity of sulphuric acid, and the liquid is mixed with ammonia and precipitated by water. (Mitscherlich.) — 2. Hydrochloric acid gas is passed through a boiling alcoholic solution of nitrobenzoic acid, and the process completed as in the preparation of the corresponding methyl-compound. (Chancel, E. Kopp.) — 3. Benzoate of ethyl is added by drops and with constant stirring to a mixture of 1 pt. nitric acid and 2 pts. oil of vitriol, which must be kept cold; the mixture gradually poured into cold water; and the separated nitrobenzoate of ethyl filtered off and crystallised from alcohol. (List & Limpricht.) — 4. A solution of chloronitrobenzoyl in strong alcohol yields by evaporation beautiful crystals of nitrobenzoate of ethyl. (Bertagnini.)

*Properties.* Crystallises very beautifully in rhombic prisms. [Fig. 61. L.] $u : u = 122°$. (Chancel.) Melts at 70° (Mitscherlich); 47° (E. Kopp); at 42° (Chancel). Boils at 300° (Mitscherlich); at about 298°. (Chancel.) Has an aromatic odour (E. Kopp) like that of strawberries (Chancel); has a fresh and somewhat bitter taste. (E. Kopp, Chancel).

| | | | | | Chancel. |
|---|---|---|---|---|---|
| 18 C | 108 | | 55·38 | | 55·18 |
| N | 14 | | 7·18 | | 7·50 |
| 9 H | 9 | | 4·61 | | 4·82 |
| 8 O | 64 | | 32·83 | | 32·70 |
| $C^{18}NH^{9}O^{8}$ | 195 | | 100·00 | | 100·00 |

*Decompositions.* 1. With *potash-ley*, it is resolved with tolerable facility into alcohol and nitrobenzoic acid. — 2. With *ammonia*, it readily forms nitrobenzamide and alcohol:

$$C^{18}NH^9O^5 + NH^3 = C^{14}N^2H^6O^4 + C^4H^6O^2.$$

3. When treated with *hydrosulphate of ammonia*, it forms amidobenzoate of ethyl. (Chancel):

$$C^{18}NH^9O^5 + 6HS = C^{18}NH^{11}O^4 + 4HO + 6S.$$

Nitrobenzoate of ethyl is insoluble in water, but dissolves very easily in *alcohol*, especially if hot.

## Nitrohippuric Acid.

$C^{18}N^2H^8O^{10} = C^{18}XAdH^6O^8$.

BERTAGNINI. *Compt. rend.* 31, 490; also *N. J. Pharm.* 18, 351; *J. pr. Chem.* 51, 255.—*Ann. Pharm.* 78, 600; abstr. *N. J. Pharm.* 20, 71.

*Formation.* 1. By the action of nitrosulphuric acid on hippuric acid. — 2. Nitrobenzoic acid is converted into hippuric acid in the animal organism, and passes off as such in the urine. 6 grammes of nitrobenzoic acid may be taken for several days in succession without injury.

*Preparation. a. From Hippuric acid.* — The solution of hippuric acid in cold fuming nitric acid is gradually mixed with an equal volume of oil of vitriol, care being taken to prevent the liquid from getting hot; the conversion is completed in two hours without any perceptible action. The liquid is mixed with three times its volume of water,—avoiding rise of temperature, — and after 12 hours, part of the nitrohippuric acid (amounting to half the weight of the hippuric acid used) is deposited in needles; on mixing the mother-liquor with carbonate of soda till it begins to show turbidity, an additional quantity of the acid separates. The still yellowish acid is washed with cold water, converted into a potash-salt, then precipitated from the lukewarm solution by hydrochloric acid, and recrystallised from water. — *b. From Urine after the exhibition of Nitrobenzoic acid.* — The strongly acid urine remains clear when mixed with hydrochloric acid after concentration at a gentle heat; if the liquid be then shaken up with ether and a little alcohol, the ethereal solution when left to evaporate, deposits brown crystalline nodules, which, after being freed from the mother-liquor and dried upon a tile, yield brownish needles by recrystallisation from hot water. These needles are boiled for five minutes with excess of milk of lime, the filtrate decomposed by hydrochloric acid, and the nitrohippuric acid recrystallised from hot water.

*Properties.* The acid crystallises by evaporation from the alcoholic solution in silky needles, which do not suffer any diminution in weight between 100° and 150°. It melts between 150° and 160°, into a colourless liquid which crystallises on cooling.

| | | | Bertagnini. a. | Bertagnini. b. |
|---|---|---|---|---|
| 18 C | 108 | 48·21 | 48·31 | 48·27 |
| 2 N | 28 | 12·50 | 12·42 | 12·77 |
| 8 H | 8 | 3·57 | 3·66 | 3·59 |
| 10 O | 80 | 35·72 | 35·61 | 35·37 |
| $C^{18}N^{2}H^{8}O^{10}$ | 224 | 100·00 | 100·00 | 100·00 |

*Decompositions.* 1. Above 100°, it assumes a reddish colour and no longer solidifies in the crystalline form; the solution in hot water still yields on cooling crystals of the acid apparently unaltered. When gradually raised to a higher temperature, it gives off pungent cough-exciting vapours and sublimes in the crystalline form; when it is suddenly exposed to a strong heat, the odour of oil of cinnamon becomes apparent. — 2. When boiled with five times its weight of concentrated hydrochloric acid, it is at first not attacked, but after an hour it is resolved into nitrobenzoic acid and glycocol. — 3. When nitric oxide gas is passed through a solution of the acid in strong nitric acid, a large quantity of gas is given off; and if, when no more gas escapes, even on the application of heat, the liquid be neutralised with ammonia, evaporated, precipitated with solution of sulphate of copper, and the precipitate decomposed by sulphuretted hydrogen, an acid is obtained which is different from nitrohippuric acid and probably consists of benzoglycolic acid. — 4. Nitrobenzoic acid dissolves without decomposition in cold oil of vitriol; at a gentle heat, the colourless solution assumes a reddish tinge, and then on addition of water yields nitrobenzoic acid; at a stronger heat, it turns brown and nitrobenzoic acid volatilises. — 5. Heated with strong potash-ley, it immediately assumes a yellow-brown colour, and gives off ammonia; at a higher temperature, it becomes purple-red and evolves hydrogen. — 6. Heated with lime, it gives off a large quantity of ammonia and a reddish oil which sinks in water and smells like oil of cinnamon; no aniline can be obtained from this oil. — 7. Sulphuretted hydrogen has no action upon the aqueous acid, but imparts a reddish colour to the acid saturated with ammonia; and if the liquid be then supersaturated with sulphuric acid, a large quantity of sulphur separates out. Perhaps amidobenzoic acid may be formed in this reaction.

*Combinations.* The acid is somewhat more soluble in cold water than hippuric acid, and dissolves in 271 pts. of water at 23°; the solubility is increased by traces of foreign matter. In boiling water it dissolves readily, the solution becoming milky on cooling and yielding oily drops which afterwards crystallise. It dissolves easily in water containing phosphate of soda.

The *Nitrohippurates* generally crystallise in needles and are for the most part soluble in water and in alcohol. Those of the alkalies detonate when heated and diffuse an odour of oil of cinnamon; those of the heavy metals give off when heated, an oil which smells very much like oil of cinnamon.

*Nitrohippurate of Ammonia.* — The solution of the acid in ammonia suddenly becomes acid during the process of evaporation, and leaves a residue easily soluble in water and alcohol.

*Nitrohippurate of Potash.* — The hot concentrated aqueous solution of the acid is neutralised with carbonate of potash, evaporated over the water-bath, and the residue exhausted with alcohol, which when eva-

porated, leaves the salt in crystalline crusts. From boiling alcohol, it separates in distinct crystals. It has an alkaline reaction, and dissolves readily in water and in weak alcohol, sparingly in strong alcohol.

*Nitrohippurate of Soda.* — Prepared like the potash-salt. The slightly coloured crusts are washed with cold strong alcohol. The salt crystallises n needles from hot alcohol. It has an alkaline reaction, dissolves very easily in water, but is not so soluble in alcohol as the potash-salt.

*Nitrohippurate of Baryta.* — When the acid is boiled with baryta-water and the excess of baryta precipitated by carbonic acid, the salt crystallises in needles as the liquid cools.

*Nitrohippurate of Lime.* — The acid is boiled for a short time with milk of lime, filtered hot, and carbonic acid gas passed through the filtrate; the solution on cooling yields white needles which have no action upon litmus. Between 100° and 110°, it gives off 10·64 p. c. (3 At.) of water.

| | | | Bertagnini. |
|---|---|---|---|
| $C^{18}N^2H^7O^7$ | 215 | 79·63 | |
| CaO | 28 | 10·37 | 11·51 |
| 3 HO | 27 | 10·00 | 10·64 |
| $C^{18}N^2H^7CaO^{10}$ | 270 | 100·00 | |

*Nitrohippurate of Magnesia.* — When *magnesia alba* is dissolved in the hot concentrated aqueous acid, the solution yields a white crystalline mass easily soluble in water and alcohol.

*Nitrohippurate of Zinc.* — A tolerably concentrated aqueous solution of nitrohippurate of lime mixed while lukewarm with chloride of zinc, becomes filled after a while with needles which must be recrystallised from boiling water. Between 100° and 110°, the crystals give off 17·85 p. c. (6 At.) water. The salt dissolves sparingly in cold water and alcohol, somewhat more readily in the same liquids when hot. (Bertagnini.)

*Nitrohippurate of Lead.* — The aqueous solution of the lime-salt forms with nitrate of lead a white heavy precipitate which immediately becomes crystalline. The salt precipitated in the cold gives off 12·30 per cent. (5 At.) water at 100°; that which is precipitated at higher temperatures is anhydrous and very hygroscopic. (Bertagnini.)

| | *At* 100°. | | Bertagnini. |
|---|---|---|---|
| 18 C | 108·0 | 33·04 | 33·12 |
| 2 N | 28·0 | 8·58 | 8·91 |
| 7 H | 7·0 | 2·19 | 2·45 |
| Pb | 103·8 | 31·76 | 31·31 |
| 10 O | 80·0 | 24·43 | 24·21 |
| $C^{18}N^2H^7PbO^{10}$ | 326·8 | 100·00 | 100·00 |

*Ferric Nitrohippurate.* — Obtained by double decomposition. Yellow flakes soluble in boiling water.

*Nitrohippurate of Copper.* — Concentrated aqueous solutions form with sulphate of copper a copious light blue precipitate; dilute solutions solidify after a while in the crystalline form. May be purified by washing with cold water and crystallisation from hot water.

| | | | | Bertagnini. |
|---|---|---|---|---|
| $C^{18}N^2H^7O^9$ | 215·0 | 84·18 | | |
| CuO | 39·8 | 15·82 | | 15·55 |
| $C^{18}N^2H^7CuO^{10}$ | 254·8 | 100·00 | | |

The pale green alcoholic solution deposits delicate, pale blue, silky needles which give off 14·93 p. c. (5 At.) water between 100° and 110°.

*Nitrohippurate of Silver.* — The solution of the lime-salt mixed with nitrate of silver gradually yields crystals, or if highly concentrated, immediately forms a curdy precipitate which soon becomes crystalline. Slender needles which when moist quickly decompose on exposure to light, but remain unaltered if dry. It dissolves readily in hot water, and with tolerable facility in cold water and alcohol.

| | | | | Bertagnini. |
|---|---|---|---|---|
| 18 C | 108·0 | 32·62 | | 32·39 |
| 2 N | 28·0 | 8·45 | | 8·73 |
| 7 H | 7·0 | 2·11 | | 2·27 |
| Ag | 108·1 | 32·65 | | 32·76 |
| 10 O | 80·0 | 24·17 | | 23·85 |
| $C^{18}N^2H^7AgO^{10}$ | 331·1 | 100·00 | | 100·00 |

Nitrohippuric acid dissolves readily in *alcohol* and *ether*.

## Nitrobenzoate of Bibromophenyl.

$C^{26}NBr^2H^7O^6 = C^{12}Br^2H^3O,C^{14}XH^4O$.

List & Limpricht. *Ann. Pharm.* 90, 203.

*Nitrobenzoate of Bibromocarbolic acid.*

Separates as a resin when finely pulverised benzoate of bibromophenyl is gradually added to nitrosulphuric acid which is kept cold; water added to the liquid scarcely throws down anything more. Crystallises from the hot alcoholic solution on cooling in small needles united in nodular masses; from a concentrated solution, it separates as an oil.

Melts between 90° and 100°, and otherwise agrees in its external properties with nitrobenzoate of binitrophenyl.

| | | | | List & Limpricht. |
|---|---|---|---|---|
| 26 C | 156 | 38·90 | | 40·41 |
| N | 14 | 3·49 | | |
| 2 Br | 160 | 39·90 | | 41·16 |
| 7 H | 7 | 1·74 | | 2·04 |
| 8 O | 64 | 15·97 | | |
| $C^{26}NBr^2H^7O^8$ | 401 | 100·00 | | |

The benzoate of bibromophenyl used by List & Limpricht in the preparation of the substance analysed, was not quite pure.

With alcoholic potash the salt forms nitrobenzoate and bibromocarbolate of potash.

It is insoluble in *water*, and sparingly soluble in hot *alcohol*.

## Nitrobenzoate of Binitrophenyl.

$C^{26}N^3H^7O^{16} = C^{12}X^2H^3O,C^{14}XH^4O^3$.

LIST & LIMPRICHT. *Ann. Pharm.* 90, 200.

*Nitrobenzoate of Binitrocarbolic acid.*

*Formation and Preparation.* When finely pulverised benzoate of phenyl is gradually added to a mixture of 1 pt. nitric acid and 2 pts. oil of vitriol, it dissolves without evolution of red vapours, and if the acid is in large excess, the liquid remains perfectly clear, but when gradually poured into cold water, deposits a bulky yellowish precipitate. When a considerable quantity of benzoate of phenyl is added to the acid mixture, the liquid becomes suddenly mixed with small crystals; and, if these are drained on a funnel stopped with asbestos, the filtrate still yields a similar precipitate on being mixed with water. The crystals, or the mass precipitated by water, are washed with water as long as that liquid continues to take up acid, and afterwards with alcohol.

*Properties.* White inodorous, more or less crystalline powder. Becomes warm when heated, melts at 150° and solidifies into a yellow transparent glass, which becomes opaque after some time, or more quickly if heated, or by contact with a sharp body. It may be sublimed in a current of air, without previous ebullition.

| | | | | List & Limpricht. |
|---|---|---|---|---|
| 26 C | 156 | | 46·84 | 47·61 |
| 3 N | 42 | | 12·61 | |
| 7 H | 7 | | 2·10 | 2·67 |
| 16 O | 128 | | 38·45 | |
| $C^{26}N^3H^7O^{16}$ | 333 | | 100·00 | |

The substance analysed perhaps contained a portion of a compound containing only 2 At. $NO^4$, and hence the amount of carbon and hydrogen appears too large.

*Decompositions.* 1. The compound burns on platinum foil with a sooty flame, leaving a small quantity of easily combustible charcoal. When heated in a tube, it creeps up the sides and explodes. — 2. Heated with oil of vitriol, it yields nitrobenzoic acid and binitrocarbolic acid. — 3. With alcoholic potash, it forms nitrobenzoate and binitrocarbolate of potash. — 4. It dissolves with deep red colour in hydrosulphate of ammonia; and the solution evaporated over the water-bath leaves a dark violet-coloured resinous mass, which dissolves with deep purple colour, while sulphur remains behind. The hydrochloric acid solution evaporated over the water-bath, leaves deep blue nodular crystals which dissolve in water, forming a yellow solution and leaving an indigo-coloured powder. When the sulphuric acid solution is boiled with excess of oxalate of baryta or the hydrochloric acid solution with oxalate of silver, the solution yields brownish yellow needle-shaped crystals, which are obtained with less colour by recrystallisation from hot water.

## Sulphide of Nitrobenzylene.

$C^{14}NH^5O^4S^2 = C^{14}XH^5,S^2$.

BERTAGNINI. *N. Ann. Chim. Phys.* 33, 473; *Ann. Pharm.* 79, 259.

*Schwefelnitrobenzen, Hydrure de benzoile nitrosulfuré.*

When sulphuretted hydrogen is passed through an alcoholic solution of nitrobenzaldide, a whitish powder separates, which must be digested in lukewarm water, then washed and dried in the air.

Greyish white, light powder, which melts into opaque drops in boiling water. Inodorous in the cold, but when rubbed between the fingers it imparts an offensive and persistent smell. When boiled with water, it exhales vapours having an alliaceous odour.

| | | | Bertagnini. |
|---|---|---|---|
| 14 C | 84 | 50·29 | 49·96 |
| N | 14 | 8·38 | 8·50 |
| 5 H | 5 | 2·99 | 3·37 |
| 2 S | 32 | 19·17 | 19·45 |
| 4 O | 32 | 19·17 | 18·72 |
| $C^{14}NH^5S^2O^4$ | 167 | 100·00 | 100·00 |

*Decompositions.* 1. By gentle heating with ordinary *nitric acid,* it is converted into a half-fused tumefied mass, which gives off abundance of nitrous vapours and soon dissolves completely, with formation of sulphuric acid and nitrobenzaldide or nitrobenzoic acid. With red fuming nitric acid, it becomes strongly heated, even to explosion when considerable quantities are used; as the solution cools, drops of bitter almond oil separate from it, mixed with a small quantity of a yellow substance. — 2. When *ammoniacal gas* is passed over sulphide of nitrobenzylene, a large quantity of sulphuretted hydrogen escapes, even in the cold, and ternitrohydrobenzamide is formed; similarly with aqueous or alcoholic ammonia.

Sulphide of nitrobenzylene is insoluble in water. — It dissolves without blackening in warm *oil of vitriol,* whence it is precipitated by water. It does not dissolve in alcohol, but cakes together when boiled in it. It is insoluble in ether, but becomes tough and translucent when immersed in that liquid.

### *Nitro-nucleus* $C^{14}X^2H^4$.

## Binitrobenzoic Acid.

$C^{14}N^2H^4O^{12} = C^{14}X^2H^4,O^4$.

CAHOURS. *N. Ann. Chim. Phys.* 25, 30; also *J. pr. Chem.* 46, 341; *Ann. Pharm.* 69, 241.

*Dinitrobenzoic acid.*

When a mixture of fuming nitric acid and oil of vitriol is heated to between 50° and 60°, and fused benzoic acid added by small portions, a

small quantity of gas is immediately given off and the benzoic acid dissolves. After the solution is complete, the liquid is gently warmed for about an hour, and as soon as it begins to show turbidity, it is cooled and mixed with water, the separated yellowish flakes washed with water till the wash-water no longer shows any acid reaction, then pressed between paper and recrystallised from boiling alcohol. If the heating with nitrosulphuric acid has not been continued long enough, the product must be again boiled with it. (Cahours.) According to Voit (*Ann. Pharm.* 99, 100) the mixture requires to be boiled for six hours, and the conversion is known to be complete by the liquid ceasing to give off red fumes: if the solution be then left to cool, the binitrobenzoic acid separates almost completely in shining crystals; but if the boiling be longer continued, vapours are given off which excite coughing, the liquid acquires a darker colour, and the acid which then separates on cooling is also coloured.

The acid separates from its alcoholic solution by sudden cooling in iridescent laminæ; by spontaneous evaporation from a dilute alcoholic solution, in short prisms having a strong lustre. It melts at a gentle heat, and when cautiously heated sublimes without decomposition in delicate needles. (Cahours.)

| | | | Cahours. |
|---|---|---|---|
| 14 C | 84 | 39·56 | 39·52 |
| 2 N | 28 | 13·34 | 13·37 |
| 4 H | 4 | 1·88 | 2·02 |
| 12 O | 96 | 45·22 | 45·09 |
| $C^{14}N^2H^4O^{12}$ | 212 | 100·00 | 100·00 |

Binitrobenzoic acid is converted by sulphuretted hydrogen into biamidobenzoic acid, $C^{14}Ad^2H^4O^4$. — Heated with alcohol and oil of vitriol, it yields binitrobenzoate of ethyl. (Voit.)

The acid dissolves very sparingly in cold, more abundantly in boiling *water*, and the solution yields delicate needles on cooling. (Cahours.) Less soluble in water than nitrobenzoic acid. (Voit.) Dissolves without decomposition in *oil of vitriol;* at a higher temperature decomposition takes place. — It dissolves abundantly in hot *nitric acid* and separates on cooling in hard shining crystals.

*Binitrobenzoate of Ammonia.* — The solution of the acid in aqueous ammonia yields on evaporation slender needles which have a silky lustre when dry. Dissolves readily in water, especially when hot.

| | | | Cahours. |
|---|---|---|---|
| 14 C | 84 | 36·68 | 36·55 |
| 3 N | 42 | 18·34 | 18·52 |
| 7 H | 7 | 3·06 | 3·14 |
| 12 O | 96 | 41·92 | 41·79 |
| $C^{14}X^2H^3(NH^4)O^4$ | 229 | 100·00 | 100·00 |

The *potash* and *soda-salts* behave like the ammonia-salt. (Cahours.) The acid dissolves with red colour in carbonate of soda. (Voit.)

*Binitrobenzoate of Baryta.* — When the acid is boiled with water and carbonate of baryta and the liquid filtered hot, the baryta salt separates on cooling in yellowish crystalline nodules.

| | *Dried at* 100°. | | Voit. |
|---|---|---|---|
| $C^{14}N^2H^2O^{11}$ | 203·0 | 72·63 | |
| BaO | 76·6 | 27·37 | 27·27 |
| $C^{14}X^2H^2Ba,O^4$ | 279·6 | 100·00 | |

*Binitrobenzoate of Lead,* obtained by double decomposition, is sparingly soluble in water.

*Binitrobenzoate of Silver.* — Obtained from the ammonia-salt by double decomposition.

| | | | Cahours. |
|---|---|---|---|
| $C^{14}N^2H^2O^{12}$ | 211·0 | 66·13 | |
| Ag | 108·1 | 33·87 | 33·75 |
| $C^{14}X^2H^2AgO^4$ | 319·1 | 100·00 | |

Binitrobenzoic acid dissolves with tolerable facility in cold *alcohol* and *ether*, easily in the same liquids when hot. (Cahours.)

## Binitrobenzoate of Ethyl.

$C^{18}N^2H^8O^{12} = C^4H^6O,C^{14}X^2H^2O^8$.

CAHOURS. *N. Ann. Chim. Phys.* 25, 30; *J. pr. Chem.* 46, 341; *Ann. Pharm.* 69, 241.
VOIT. *Ann. Pharm.* 99, 105.

When absolute alcohol is saturated with binitrobenzoic acid, an oil separates which solidifies on cooling, and of which an additional quantity is precipitated by water. The product is washed with water containing ammonia, and crystallised from hot alcohol. (Cahours.) — Binitrobenzoic acid heated with alcohol and oil of vitriol yields the ether in oily drops which solidify on cooling, and may be crystallised from hot alcohol whence it separates in a magma of long silky needles. (Voit.)

Long, slender needles, having a strong lustre and scarcely perceptible yellow colour.

| | | | Cahours. |
|---|---|---|---|
| 18 C | 108 | 45·00 | 44·74 |
| 2 N | 28 | 11·67 | 11·58 |
| 8 H | 8 | 3·33 | 3·44 |
| 12 O | 96 | 40·00 | 40·24 |
| $C^{18}N^2H^8O^{12}$ | 240 | 100·00 | 100·00 |

By strong *potash-ley,* especially when hot, it is quickly decomposed into alcohol and binitrobenzoic acid. — By digestion for several days

in *alcoholic ammonia*, the ether is converted into *binitrobenzamide*, $C^{14}X^2AdH^3,O^2$. — *Sulphuretted hydrogen* passed through the hot ammoniacal solution of the ether, converts it, with separation of silver, into *biamidobenzoic acid* $C^{14}H^4Ad^2,O^4$. — When the ether is digested with sulphide of ammonium, a large quantity of sulphur separates, and the filtrate leaves on evaporation a crystalline mass which is probably biamidobenzamide. (Voit.)

*Oxynitro-nucleus* $C^{14}XH^4O$.

## Anhydrous Nitrobenzoic Acid.

$C^{14}XH^4O^7 = C^{14}XH^4O,O^2$.

GERHARDT. *N. Ann. Chim. Phys.* 37, 321; *Ann. Pharm.* 87, 158.

8 pts. of dry nitrobenzoate of soda are heated to 150° with 1 pt. of chlorophosphoric acid, till the odour of chloride of benzoyl is no longer perceptible. After washing with cold water, there remains a white mass nearly insoluble in boiling alcohol or ether, less fusible than nitrobenzoic acid, but quickly converted into the latter when washed.

## Anhydrous Benzo-nitrobenzoic Acid.

$C^{28}NH^9O^{10} = C^{14}XH^4O^3,C^{14}H^5O^3$.

GERHARDT. *N. Ann. Chim. Phys.* 37, 321; *Ann. Pharm.* 87, 158.

*Benzoic Nitrobenzoate, Benzo-nitrobenzoic Anhydride, Benzoate of Nitrobenzoyl, Nitrobenzoate of Benzoyl.*

5 pts. of chloride of benzoyl are heated with 7 pts. of dry benzoate of soda, and the syrupy product, which crystallises on cooling, is heated with a small quantity of water, washed with carbonate of soda, and dissolved in hot alcohol, whence the anhydride separates in the crystalline form on cooling. It is more stable than the preceding compound.

*Chloronitro-nucleus* $C^{14}ClXH^4$.

## Chloride of Nitrobenzoyl.

$C^{14}ClNH^4O^6 = C^{14}ClXH^4,O^2$ [$= C^{14}XH^4O^2,Cl$].

CAHOURS. *N. Ann. Chim. Phys.* 23, 339; also *J. pr. Chem.* 45, 138.
BERTAGNINI. *N. Ann. Chim. Phys.* 33, 465; also *Ann. Pharm.* 79, 259.

*Chloronitrobenzoyl, Chlorure de benzoile nitrique.*

*Formation and Preparation.* 1. Nitrobenzaldide exposed to the action of chlorine gas in sunshine is quickly converted into chloride of nitrobenzoyl. (Bertagnini.) — 2. When nitrobenzoic acid is gently heated with pentachloride of phosphorus, a violent action takes place, and a yellowish liquid passes over into the receiver. The boiling point

of this distillate rises from 108°, at which temperature chlorophosphoric acid distils over, till it reaches 270°. The last portion is washed with cold water, dried over chloride of calcium and rectified. (Cahours.)

*Properties.* Yellow, mobile liquid, heavier than water. Boils between 265° and 268°. (Cahours.) Smells like chloride of benzoyl. (Bertagnini.)

| | | | Cahours. |
|---|---|---|---|
| 14 C | 84·0 | 45·25 | 45·06 |
| N | 14·0 | 7·63 | 7·39 |
| 4 H | 4·0 | 2·15 | 2·34 |
| Cl | 35·4 | 19·08 | 18·40 |
| 6 O | 48·0 | 25·89 | 26·81 |
| $C^{14}NH^4ClO^6$ | 185·4 | 100·00 | 100·00 |

*Decompositions.* 1. Chloride of nitrobenzoyl is insoluble in water, but is gradually converted into nitrobenzoic acid by water or moist air. — 2. When heated with *potash*, it is quickly decomposed, yielding chloride of potassium and nitrobenzoate of potash. — 3. With *ammoniacal gas* it becomes heated and forms a white crystalline mass possessing the properties of nitrobenzamide. (Cahours, Bertagnini.) The same reaction appears to take place with aqueous ammonia. (Bertagnini.) — 4. With *wood-spirit*, it becomes heated and forms a solution which soon deposits crystals of nitrobenzoate of methyl. (Bertagnini.) — It dissolves with rise of temperature in strong *alcohol*, and the solution when evaporated yields, besides hydrochloric acid, beautiful crystals of nitrobenzoate of ethyl. (Bertagnini.) — 6. With *aniline*, it rapidly evolves hydrochloric acid gas, and forms a solid mass which crystallises from alcohol in shining needles and doubtless consists of nitrobenzanilide. (Bertagnini.)

The compound dissolves without alteration in *ether*, even at the boiling point, and remains in drops when the ether evaporates.

## ¶. Chloronitrobenzoic Acid.

$C^{14}ClNH^4O^8 = C^{14}ClXH^4,O^4$.

LIMPRICHT & V. USLAR. *Ann. Pharm.* 102, 261.

*Nitrochlorbenzoesäure.*

Chlorobenzoic acid dissolves slowly in fuming nitric acid, and the solution if mixed with water after a few hours, does not yield any immediate precipitate, but continues for several days to deposit transparent colourless plates of chloronitrobenzoic acid.

The crystals dissolve readily in alcohol and ether, and from the ethereal solution the acid crystallises in prisms. In water it melts when warmed, and dissolves at the boiling heat, but does not separate out again on cooling. The dry acid melts at 118°.

*Chloronitrobenzoate of Baryta.* — $C^{14}ClXH^3BaO^4 + 2Aq$. — Very soluble, nodular crystals which give off 6·4 p.c. (2 At.) water at 100°.

| | At 100°. | | Limpricht & v. Uslar. |
|---|---|---|---|
| $C^{14}ClNH^3O^3$ | 200·4 | 74·5 | |
| Ba | 68·6 | 25·5 | 25·6 |
| $C^{14}ClXH^3BaO^4$ | 269·0 | 100·0 | |

*Chloronitrobenzoate of Silver.* — $C^{14}ClXH^3AgO^4 + Aq$? — Nitrate of silver added to the concentrated solution of the acid, throws down small shining laminæ, which do not blacken when the liquid is boiled, and dissolve pretty readily in water.

| | | | Limpricht & v. Uslar. |
|---|---|---|---|
| $C^{14}ClNH^3O^8$ | 200·4 | 63·1 | |
| Ag | 108·1 | 34·1 | 33·8 |
| HO | 9·0 | 2·8 | |
| $C^{14}ClXH^3AgO^8 + Aq$ | 317·5 | 100·0 | |

*Chloronitrobenzoate of Ethyl.* — Chlorobenzoate of ethyl (p. 115) dissolves in a mixture of 2 pts. oil of vitriol and 1 pt. strong nitric acid, and the solution mixed with water after 24 hours, deposits an oil which crystallises after a while and doubtless consists of chloronitrobenzoate of ethyl. It dissolves in alcohol, and separates from in solution in large, transparent, colourless crystals. (Limpricht & v. Uslar.) ¶.

*Amidogen-nucleus* $C^{14}AdH^6$.

## Benzamide.

$C^{14}NH^7O^2 = C^{14}AdH^6,O^2$.

WÖHLER & LIEBIG. (1832,) *Ann. Pharm.* 3, 268; also *Pogg.* 26, 465.
WINCKLER. *Repert.* 48, 206.
FEHLING. *Ann. Pharm.* 28, 48.
SCHWARZ. *Ann. Pharm.* 75, 195.
LAURENT. *Rev. scientif.* 16, 391.
DESSAIGNES. *N. Ann. Chim. Phys.* 34, 146; also *Ann. Pharm.* 82, 234; also *J. pr. Chem.* 55, 432.
GERHARDT & CHIOZZA. *Gerh. Traité.* 3, 268.

*Formation.* 1. By heating anhydrous benzoic acid with ammonia. (Gerhardt, p. 95) — 2. By the action of ammonia on bromide, chloride or cyanide of benzoyl. (Wöhler & Liebig.) By the action of chloride of benzoyl on carbonate of ammonia. (Gerhardt.) — 3. Benzoate of ethyl in contact with aqueous ammonia forms benzamide, slowly at ordinary temperatures, more quickly at 100° in a sealed tube. (Dumas, *Compt. rend.* 25, 734.) — 4. By boiling hippuric acid with water and peroxide of lead. (Fehling.)

*Preparation.* — 1. Chloride of benzoyl absorbs dry ammoniacal gas with very great rise of temperature, and becomes converted into a white

solid mass of sal-ammoniac and benzamide, which must be repeatedly comminuted, in order that none of the chloride of benzoyl may be enclosed within it and so escape the action of the ammonia. The sal-ammoniac is extracted by cold water and the benzamide crystallised from boiling water. Under certain circumstances, especially when the chloride of benzoyl contains excess of chlorine, there is formed, on saturating the liquid with ammonia, an oily body having the odour of bitter almonds, which imparts to the benzamide the property of melting into an oil before dissolving when heated with water, and separating again from the solution in oily drops which do not solidify till after some time. If the quantity of ammonia passed into the chloride of benzoyl is not sufficient to complete the reaction, the benzamide, when treated with water, is decomposed by the hydrochloric acid resulting from the decomposition of the chloride of benzoyl. (Wöhler & Liebig.) — 2. When an alcoholic solution of chloride of benzoyl is mixed with aqueous ammonia, a copious crystalline precipitate is somewhat quickly formed, consisting of benzamide, which may be purified by pressure and repeated crystallisation. (Laurent.) — 3. Chloride of benzoyl is triturated with excess of commercial carbonate of ammonia; the mixture gently heated and then washed with cold water; and the residual benzamide crystallised from boiling water or alcohol. (Gerhardt.)

4. Bitter almond water is distilled with hydrochloric acid; the distillate mixed with strong hydrochloric acid; and the liquid evaporated over the water-bath. The residue is a thick oil, which, on cooling, solidifies into a soft crystalline mass; and this, when exhausted with cold ether and several times washed, leaves a greyish white residue, which is obtained pure by crystallisation from hot alcohol.—Benzamide may also be obtained from the residue of the distillation of bitter almond water with hydrochloric acid. (Winckler.)

5. Hippuric acid is boiled with water and peroxide of lead, and the resulting hippurate of lead decomposed from time to time by dilute sulphuric acid, avoiding an excess. When the evolution of carbonic acid has ceased, and the oxide of lead still in excess remains unaltered, the solution is filtered hot; the filtrate decanted from any hippuric acid that may crystallise out before cooling, and evaporated; the white granular residue dissolved in water; and the solution filtered from any hipparaffin that may be present; the filtrate then yields, on cooling and further evaporation, indistinct crystals of benzamide. (Fehling, Schwarz.)

*Properties.* When a hot aqueous solution of benzamide is left to cool slowly, the entire liquid solidifies to a white mass consisting of fine needles having a silky lustre. After a day or more, separate cavities form in this mass, containing one or more large crystals into which the silky modification has been converted. This transformation extends gradually through the entire mass. When the boiling solution is slowly cooled, the benzamide separates in laminæ having a pearly lustre. (Wöhler & Liebig.) — The finest crystals are obtained from a solution in weak ammonia or potash; such a solution, when sufficiently concentrated, solidifies on cooling in a mass of slender needles, which gradually change into large shining crystals. The aqueous solution yields only the latter. (Schwarz.) — Transparent right rhombic prisms having a strong pearly lustre; the oblique lateral edges are truncated by a face to which the cleavage-plane is parallel, and on which the bevelling-faces are set at right angles. (Wöhler & Liebig.) Large oblique rectangular table (Fig. 92). $i : t = 103° 30'$; $t : m = 117°$; $t$ is rectangular and predominates; $i$ and $m$ are very narrow. (Laurent.) Inodorous. Melts at

115° (at 100° according to Schwarz), forming a transparent colourless liquid which on cooling solidifies in a crystalline mass composed of large laminæ and frequently penetrated with cavities enclosing well defined crystals. (Wöhler & Liebig.) — Volatilises a little above its melting point. (Schwarz.) May be distilled without alteration and gives off vapours having a faint odour of bitter almonds. (Wöhler & Liebig.) The contents of the retort turn brown during the distillation. (Schwarz.) Its taste is faintly bitter and aromatic. (Schwarz.)

| | | | Wöhler & Liebig. | Fehling. | Schwarz. |
|---|---|---|---|---|---|
| 14 C | 84 | 69·42 | 68·92 | 68·75 | 69·19 |
| N | 14 | 11·56 | 11·56 | 11·02 | 11·21 |
| 7 H | 7 | 5·78 | 5·79 | 5·80 | 6·06 |
| 2 O | 16 | 13·24 | 13·73 | 14·43 | 13·54 |
| $C^{14}NH^7O^2$ | 121 | 100·00 | 100·00 | 100·00 | 100·00 |

= $NH^2,C^{14}H^5O^2$ = ammonia in which 1 At. H is replaced by benzoyl.

*Decompositions.* 1. Benzamide is very inflammable and burns with a sooty flame. — 2. The vapours passed through a narrow red-hot tube, pass over for the most part undecomposed, and without deposition of charcoal; but the benzamide which passes over is mixed with a peculiar oil, which is lighter than water, and insoluble therein, has a sweetish aromatic odour and very sweet taste, burns with a bright flame, and is not decomposed by acids, alkalis, or potassium. (Wöhler & Liebig.) — The vapours of benzamide passed through a tube filled with pumice-stone, yield at a moderate heat, hydrogen, nitrogen, carbonic oxide and benzol. (Barreswil & Boudault, *N. J. Pharm.* 5, 268.) — 3. Benzamide dissolves in strong *acids* at the boiling heat, and the solution on cooling deposits crystals of benzoic acid, the liquid retaining the ammonia-salt of the acid employed. — 4. By the action of *pentachloride of phosphorus* on benzamide, benzonitrile is produced. (Cahours, *Compt. rend.* 25, 725);

$$C^{14}NH^7O^2 + PCl^5 = C^{14}NH^5 + PCl^3O^2 + 2HCl.$$

5. Benzamide boiled with aqueous *potash* gives off ammonia and forms benzoate of potash. (Wöhler & Liebig.) Dilute alkalies do not act on benzamide even when heated with it. (Schwarz.) — 6. Anhydrous *baryta* heated with benzamide, is brought into a kind of fusion, and appears to be converted into hydrate; at the same time ammonia is given off, together with the sweetish oil produced in (2). (Wöhler & Liebig.) — 7. When benzamide is fused with *potassium*, no ammonia is evolved, but cyanide of potassium is formed together with the sweetish oil just mentioned. (Wöhler & Liebig.) — The formation of cyanide of potassium in this case is due to a secondary reaction. (Dumas, Malaguti & Leblanc, *Compt. rend.* 25, 660.) — 8. When benzamide is boiled with *peroxide of lead* and *sulphuric* or *hydrochloric acid*, a colourless filtrate is obtained which when mixed with ammonia and exposed to air, turns brown and deposits a mould-like substance. (Schwarz.) — When benzamide is heated with 2 At. of *benzoic anhydride*, benzoic acid and benzonitrile are produced;

$$C^{14}NH^7O^2 + 2C^{14}H^5O^3 = 2C^{14}H^6O^4 + C^{14}NH^5.$$

10. Benzamide heated with *chloride of benzoyl* yields benzoic acid, benzonitrile and hydrochloric acid. (Gerhardt & Chiozza):

$$C^{14}NH^7O^2 + C^{14}H^5ClO^2 = C^{14}H^6O^4 + C^{14}NH^5 + ClH.$$

*Combinations.* Benzamide dissolves very sparingly in cold, but abundantly in boiling *water.*

*Benzamide with Bromine.* — $C^{14}AdH^5O^2 + 2Br$. — Benzamide dissolves in bromine without evolution of hydrobromic acid. After 14 days in winter, the liquid deposits ruby-coloured crystals which gradually give off bromine on exposure to the air, and are decomposed slowly by water, immediately by ammonia, with separation of benzamide. (Laurent.)

| | | | Laurent. |
|---|---|---|---|
| $C^{14}NH^7O^2$ | 121 | 43·06 | |
| 2 Br | 160 | 56·94 | 56·3 |
| $C^{14}NH^7O^2,2Br$ | 281 | 100·00 | |

*With Hydrochloric Acid.* — Benzamide dissolves readily in warm concentrated hydrochloric acid, and the solution on cooling deposits long aggregated prisms, which exhale hydrochloric acid on exposure to the air, and give off the whole of that acid in a few days, becoming opaque at the same time. After recent pressing between paper, they contain 20·46 per cent. of hydrochloric acid; (the formula $C^{14}NH^7O^2,HCl$ requires 23·17 per cent). (Dessaignes.)

The aqueous solution of benzamide dissolves small quantities of oxide of copper and oxide of silver. It dissolves *mercuric oxide* in large quantity, and the saturated solution solidifies in a crystalline mass. If the mass coloured by excess of mercuric oxide be treated with hot alcohol, the solution filtered from the mercuric oxide yields on cooling, white shining laminæ, which may be washed and dried at 100°. (Dessaignes.)

| | | | Dessaignes. |
|---|---|---|---|
| $C^{14}NH^6O$ | 113 | 50·91 | |
| HgO | 108 | 49·09 | 49·12 |
| $C^{14}NH^6HgO^2$ | 221 | 100·00 | |

Chloride of benzoyl acts on this compound with great violence, even if artificially cooled, producing benzoic acid, benzonitrile and chloride of mercury. (Gerhardt & Chiozza);

$$C^{14}NH^6HgO^2 + O^{14}H^5ClO^2 = C^{14}H^6O^4 + C^{14}NH^5 + HgCl.$$

Benzamide dissolves readily in *alcohol* and in boiling *ether*, whence it separates in beautiful crystals (Wöhler & Liebig.)

## Amidobenzoic Acid.

$C^{14}NH^7O^4 = C^{14}AdH^5,O^4$.

Zinin. (1845.) *J. pr. Chem.* 36, 103.
Chancel. *Compt. rend.* 28, 422.
Gerland. *Ann. Pharm.* 86, 143; 91, 185.
Voit. *Ann. Pharm.* 99, 100; *Chem. Soc. Qu. J.* 9, 268.

*Benzamic Acid, Carbanilic acid.*—Gerland showed in 1853 that amidobenzoic and carbanilic acids are identical, but differ from anthranilic acid which is isomeric with them.—The term benzamic, generally applied to this acid, is inappropriate, because it is not really the amidogen-acid of benzoic acid; in fact, it is only the radicals of bibasic acids that can form amidogen acids properly so-called (vid. Gerhardt, *Traité*, iv, 668).

*Formation and Preparation.* *a.* (*Amidobenzoic acid.*)—1. When an alcoholic solution of nitrobenzoic acid is saturated with ammonia and sulphuretted hydrogen and then boiled, the liquid acquires an olive-green colour, then becomes turbid and deposits a large quantity of sulphur, and ultimately becomes transparent and of a yellow colour. In order to decompose the nitrobenzoic acid completely, the liquid is decanted from the sulphur; again mixed with the alcoholic hydrosulphate of ammonia which has been distilled off; once more saturated with sulphuretted hydrogen; and several times distilled. This series of operations is repeated two or three times till no more sulphur separates. The residual alcoholic liquid is mixed with water; boiled to expel completely the alcohol and sulphuretted hydrogen; then evaporated to a syrup and supersaturated with strong acetic acid, whereupon it solidifies to a thick yellow pulp, which is left to drain on a filter, pressed between paper, dried on a tile, dissolved in hot water, decolorised by animal charcoal, and filtered at the boiling heat. (Zinin.)—2. Gerland dissolves nitrobenzoic acid in excess of aqueous ammonia, saturates with sulphuretted hydrogen, and boils the liquid, keeping it all the while excluded as completely as possible from the air, and passing sulphuretted hydrogen through it till that gas is no longer absorbed. The solution decanted from the separated sulphur and neutralised with acetic acid, deposits nearly colourless amidobenzoic acid, which may easily be obtained pure by repeated crystallisation from water.—¶ 3. Nitrobenzoic acid is digested with iron filings and acetic acid, whereupon a brisk action takes place attended with rise of temperature; the mass is then heated for some time over the water-bath, digested with aqueous carbonate of soda, and filtered; the filtrate neutralised with acetic acid, and precipitated with acetate of lead; the resulting precipitate of amidobenzoate of lead decomposed by sulphuretted hydrogen; and the acid obtained in the crystalline state as above. Ferrous acetate appears to exert upon nitro-acids in general the same reducing action as hydrosulphate of ammonia. (Boullet, *Compt. rend.* 43, 399; see also Schiff, *Ann. Pharm.* 101, 94.)

*b.* (*Carbanilic acid.*)—Carbanilamide (xi, 303) is boiled with strong potash-ley as long as ammonia continues to escape. If the liquid be then supersaturated with acetic acid, the carbanilic acid crystallises out on cooling. (Chancel.)

*Properties.* Small white crystalline nodules and spherules. Has a rather sweet and sourish taste and reddens litmus strongly. (Zinin.) Orange-yellow needles. (Chancel.)—The acid prepared according to *a*, 1, is obtained in needles by evaporating its solution to dryness with potash and precipitating the redissolved salt with acetic acid, or by heating its solution or that of one of its salts somewhat above 100°. The acid prepared according to *b*, crystallises in nodules from the ammoniacal solution after addition of acetic acid. By the process *a*, 2, it is obtained in hard crystalline masses or transparent needles. (Gerland.)

| | | | Zinin. |
|---|---|---|---|
| 14 C | 84 | 61·32 | 61·06 |
| N | 14 | 10·22 | 10·01 |
| 7 H | 7 | 5·11 | 5·13 |
| 4 O | 32 | 23·35 | 23·80 |
| $C^{14}AdH^{5}O^{4}$ | 137 | 100·00 | 100·00 |

*Decompositions.* 1. Amidobenzoic acid in the state of solution quickly decomposes when exposed to the air and yields a brown resinous substance. (Zinin.) — 2. When heated, it melts, gives off white irritating vapours having the odour of benzoic acid, and leaves a bulky easily combustible charcoal; part of the acid sublimes undecomposed. (Zinin.) — 3. Carbanilic acid heated with spongy platinum is resolved into aniline and carbonic acid. (Chancel.) — 4. It is not attacked by ordinary *nitric acid* at the boiling heat; in fuming nitric acid it dissolves with blood-red colour, and on boiling gives off red vapours, the liquid turning yellow and being afterwards no longer precipitated by water. The liquid neutralised with ammonia forms with lead-salts, an ochre-yellow precipitate, with copper-salts, a green, and with silver-salts a red-brown precipitate. (Zinin.) Fuming nitric acid converts amidobenzoic acid into picric acid. (Gerland.) — 5. When *nitrous acid* is passed into an aqueous solution of amidobenzoic acid, nitrogen gas free from carbonic acid is evolved, and a red amorphous precipitate formed, which becomes scarlet when dry, is insoluble in water and alcohol, cakes together in resinous lumps when boiled with water, but is dissolved with red colour by caustic alkalies or their carbonates, and reprecipitated in its original state by acids. This precipitate contains from 58·0 to 59·8 per cent. of carbon and from 3·9 to 3·4 per cent. of hydrogen. Its solution in ammonia forms with acetate of lead, sulphate of copper and nitrate of silver, brown amorphous precipitates; the lead-compound contains from 38 to 49 per cent. of lead-oxide; the silver compound, from 41·9 to 51·5 of silver-oxide. — The red precipitate dissolves in strong acids and is precipitated without alteration by water. — If the action of the nitrous acid be longer continued, complete solution takes place; and the red-brown liquid, which has an unpleasant, somewhat bitter taste, yields after being evaporated to a syrup, crystals of oxybenzoic acid ($C^{14}H^{6}O^{6}$) having a fine yellow colour. (Gerland.) — 6. Amidobenzoic acid forms with cold *oil of vitriol* a colourless solution, which turns yellow when heated, is decolorised by addition of water, and when neutralised, yields with cupric salts a precipitate having the green colour of malachite. (Zinin.) — With oil of vitriol it forms sulphanilic acid. (Chancel, Gerland.) — 7. Amidobenzoic acid boiled with water and *peroxide of manganese* is converted into benzoic acid. The liquid acquires an intense red colour and gives off nitrogen gas together with traces of carbonic acid: and if, after several days boiling, the colouring matter be precipitated by acetate of lead, the filtered solution deposits on cooling crystals of benzoate of lead. A similar action but much more rapid is produced by *permanganate of potash.* (Gerland.) — 8. A mixture of *chromate of potash* and *sulphuric acid* acts with great violence on amidobenzoic acid; the evolved gases certain carbonic acid. (Gerland.) — 9. Hot aqueous amidobenzoic acid absorbs *chlorine gas* in large quantity, and the saturated liquid contains hydrochloric acid and benzoic acid. Amidobenzoic acid dissolved in alcohol is converted by chlorine into a black resinous substance which is insoluble in water, dissolves with deep violet colour in alcohol, and forms sparingly soluble saline compounds with metallic oxides. (Zinin.)

*Combinations.* Amidobenzoic acid dissolves sparingly in cold, abundantly in boiling water. (Zinin.)

*Sulphate of Amidobenzoic acid.* — Dry amidobenzoic acid dissolves with evolution of heat in oil of vitriol, and forms a colourless liquid which may be heated to the boiling point without decomposing, and on cooling solidifies in a mass consisting of needles having a diamond lustre; by repeated crystallisation from hot water or alcohol, the compound may be obtained colourless. It remains unaltered in contact with the air. The solution has an intensely sweet taste. (Gerland.)

| | | | Gerland. |
|---|---|---|---|
| 14 C | 84 | 41·2 | 42·3 |
| N | 14 | 6·8 | 6·5 |
| 10 H | 10 | 4·9 | 4·9 |
| S | 16 | 7·9 | 8·3 |
| 10 O | 80 | 39·2 | 38·0 |
| $C^4NH^7O^4,SO^4H + 2Aq$ | 204 | 100·0 | 100·0 |

By hot water it is gradually resolved into sulphuric and amidobenzoic acids. With bases it yields a sulphate and an amidobenzoate. (Gerland.)

*Nitrate of Amidobenzoic acid.* — Amidobenzoic acid dissolves in heated nitric acid without evolution of gas; and on cooling, the compound separates in small crystalline scales. The excess of nitric acid is evaporated over the water bath and the residue repeatedly crystallised from water. Thin laminæ permanent in the air, and easily soluble in water and alcohol. The aqueous solution gives with sulphuric acid and protosulphate of iron, the reaction of nitric acid.

| | | | Gerland. |
|---|---|---|---|
| 14 C | 84 | 42 | 41·7 |
| 2 N | 28 | 14 | |
| 8 H | 8 | 4 | 4·3 |
| 10 O | 80 | 40 | |
| $C^{14}NH^7O^4,NO^6H$ | 200 | 100 | |

*Hydrochlorate.* — On adding strong hydrochloric acid to the liquid obtained by treating nitrobenzoic acid with sulphide of ammonium, after it has been decanted from the precipitated sulphur and evaporated, hydrochlorate of amidobenzoic acid separates in needles united in nodular groups. (Voit.) — With bichloride of platinum it forms the platinum-salt $C^{14}NH^7O^4,HCl,PtCl^2$. (Cahours, *Ann. Pharm.* 103, 88.)

Amidobenzoic acid expels carbonic acid from its compounds. The *amidobenzoates* are for the most part soluble in water, and crystallisable. The amidobenzoates of the alkalis heated with hydrate of potash or lime, give off carbonic acid and aniline (Chancel), and a large quantity of ammonia. (Gerland.)

¶. *Amidobenzoate of Soda.* $C^{14}AdH^4NaO^4$. — The hot aqueous solution of the baryta-salt is precipitated by an equivalent quantity of sulphate of soda; the filtrate evaporated nearly to dryness; the residue mixed with alcohol; and the resulting white crystalline magma pressed between paper and dried at 100°. When examined by the microscope it appears to consist of needle-shaped crystals. (Voit.)

| | At 100°. | | Voit. |
|---|---|---|---|
| $C^{14}NH^{6}O^{3}$ | 128 | 80·45 | |
| NaO | 31 | 19·55 | 19·18 |
| $C^{14}NH^{6}NaO^{4}$ | 159 | 100·00 | |

*Amidobenzoate of Baryta*, $C^{14}AdH^{4}BaO^{4}$. — The aqueous solution of hydrochlorate of amidobenzoic acid is digested with carbonate of baryta till the acid reaction disappears, and the hot-filtered liquid is evaporated over the water-bath; it then, at a certain degree of concentration, deposits large pale reddish prisms, which cannot be completely decolorized even by repeated crystallisation, but nevertheless yield a perfectly white powder. (Voit.)

| | At 100°. | | Voit. |
|---|---|---|---|
| 14 C | 84·0 | 41·07 | 41·12 |
| N | 14·0 | 2·93 | 3·51 |
| 6 H | 6·0 | 33·50 | 33·29 |
| Ba | 68·5 | 6·84 | |
| 4 O | 32·0 | 15·66 | |
| $C^{14}NH^{6}BaO^{4}$ | 204·5 | 100·00 | |

*Amidobenzoate of Strontia*, — $C^{14}AdH^{4}SrO^{4}+2Aq$. — The aqueous solution of the baryta-salt is precipitated with sulphuric acid; the filtrate mixed with a sufficient quantity of hydrate of strontia to produce a slight alkaline reaction, and evaporated. It then yields prismatic crystals which have a faint reddish colour, but may be decolorised by recrystallisation from alcohol. They give off 8·78 p.c. (2 At.) water at 100°, and are easily soluble in water, sparingly in alcohol. (Voit.)

| | At 100°. | | Voit. |
|---|---|---|---|
| $C^{14}NH^{6}O^{3}$ | 128 | 71·11 | |
| SrO | 52 | 28·89 | 28·58 |
| $C^{14}NH^{6}SrO^{3}$ | 180 | 100·00 | |

*Amidobenzoate of Lime.* $C^{14}AdH^{4}CaO^{4}$. — When hydrochlorate of amidobenzoic acid is boiled with milk of lime and the filtrate evaporated, the concentrated liquid yields delicate white needles which turn red on exposure to the air. They are purified by repeated crystallisation from hot alcohol, and pressure between paper. (Voit.)

| | At 100°. | | Voit. |
|---|---|---|---|
| $C^{14}NH^{6}O^{3}$ | 128 | 82·05 | |
| CaO | 28 | 17·95 | 17·61 |
| $C^{14}NH^{6}CaO^{4}$ | 156 | 100·00 | |

*Amidobenzoate of Magnesia.* $C^{14}AdH^{4}MgO^{4}+7Aq$. — Obtained by decomposing the baryta-salt with sulphate of magnesia. Large, transparent, six-sided prisms with oblique truncated faces. After drying over sulphuric acid they give off 29·36 p.c. (7 At.) water at 100°.

| | At 100°. | | Voit. |
|---|---|---|---|
| $C^{14}NH^6O^3$ | 128·0 | 86·08 | |
| MgO | 20·7 | 13·92 | 13·54 |
| $C^{14}NH^6MgO^7$ | 148·7 | 100·00 | |

The salt decomposes rapidly when exposed to the air. (Voit.) ¶.

With *protoxide of lead*, amidobenzoic acid forms three salts: (*a.*) Pulverulent, insoluble in water; (*b.*) Sparingly soluble needles; (*c.*) Shining needles which dissolve with greater facility.

The *copper-salt* has the colour of malachite; is insoluble in water and alcohol, but dissolves readily in the stronger acids.

*Amidobenzoate of Silver.*—Amidobenzoate of ammonia forms with nitrate of silver a white curdy precipitate which soon becomes crystalline. It dissolves in alcohol and ether more readily than in water, assumes a blue-violet tinge when immersed in boiling water, but does not dissolve (Zinin); it dissolves pretty readily in hot water, and crystallises on cooling in somewhat elongated scales. (Chancel.)

| | | | Chancel. |
|---|---|---|---|
| 14 C | 84·0 | 34·41 | 34·16 |
| N | 14·0 | 5·73 | |
| 6 H | 6·0 | 2·46 | 2·59 |
| Ag | 108·1 | 44·28 | 44·11 |
| 4 O | 32·0 | 13·12 | |
| $C^{14}AdH^4AgO^4$ | 244·1 | 100·00 | |

The salt decomposes when heated above 100°. (Chancel.) It blackens when heated, melts, swells up, gives off irritating vapours, and leaves a carbonaceous residue which easily burns away to metallic silver. (Zinin.)

## Benzimic Acid.

LAURENT. *Compt. rend.* 1, 37.

When an alcoholic solution of bitter almond oil saturated with ammonia, is mixed with water after standing for 48 hours, the water takes up benzimate of ammonia. On decanting the liquid and neutralising with hydrochloric acid, benzimic acid separates on cooling, in beautiful, slender white silky needles, which melt when heated and cannot be distilled without decomposition.

## Amidobenzoate of Methyl.

CHANCEL. *Compt. rend.* 30, 751.

*Benzamate of Methyl, Benzaminformester, Ether carbanilique de methylène, Carbanilmethylane.*

Produced by treating nitrobenzoate of ethyl with hydrosulphate of ammonia. Its properties are similar to those of amidobenzoate of ethyl.

## Amidobenzoate of Ethyl.

CHANCEL. *Compt. rend.* 30, 751.

*Benzamate of Ethyl, Benzaminvinester, Ether carbanilique de l'alcohol, Carbanilethane.*

When a small quantity of hydrosulphate of ammonia is added to an alcoholic solution of nitrobenzoate of ethyl, a copious precipitation of sulphur takes place; and on adding water to the liquid, after it has been heated to complete the decomposition, amidobenzoate of ethyl is precipitated in the form of a colourless oil, which may be purified by repeated solution in alcohol and precipitation by water. (Chancel.) The same reduction may be effected with metallic iron and acetic acid. (Schiff, *Ann. Pharm.* 99, 118.)

The alcoholic solution treated with potash yields amidobenzoate of potash.

## Thiobenzamide.

$C^{14}NH^7S^2 = C^{14}AdH^5,S^2$.

CAHOURS. *Compt. rend.* 27, 329; also *J. pr. Chem.* 43, 354.

*Schwefelbenzamid, Benzamide sulfuré.*

When a solution of benzonitrile in slightly ammoniacal alcohol is saturated with sulphuretted hydrogen, the liquid soon assumes a brownish yellow colour; and if, after some hours, it be boiled down to ¼ and mixed with water, it deposits yellow flakes, which dissolve in boiling water and crystallise on cooling in long sulphur-yellow needles having a silky lustre.

| | | | Cahours. |
|---|---|---|---|
| 14 C | 84 | 61·30 | 61·22 |
| N | 14 | 10·22 | 10·34 |
| 7 H | 7 | 5·11 | 5·13 |
| 2 S | 32 | 23·37 | 23·51 |
| $C^{14}NH^7S^2$ | 137 | 100·00 | 100·00 |

## ¶. Tribenzylamine.

$C^{42}NH^{21} = C^{14}Ad(C^{14}H^7)^3H^3,H^2$.

CANNIZZARO. *Cimento*, 3, 397.

When chloride of benzoyl, $C^{14}H^7Cl$, and alcoholic ammonia are heated together in a sealed tube to 100°, ammoniacal gas passed into the liquid after cooling, the resulting precipitate exhausted with ether, and the ethereal solution left to evaporate, tribenzylamine $[(C^{14}H^7)^3N,]$ is obtained in shining laminæ, which melt at 91·3° to a colourless liquid

and at 360° are partly volatilised, partly decomposed. The compound is alkaline and forms with *hydrochloric acid* a salt which is sparingly soluble in cold water, more soluble in boiling water, and crystallises from the solution in needles. The solution of this salt mixed with bichloride of platinum, forms *chloroplatinate of tribenzylamine* $C^{42}H^{21}N,HCl,PtCl^2$, which crystallises in orange-coloured needles.

Tribenzylamine dissolves sparingly in cold *water* and *alcohol*, more readily in boiling alcohol, and still more in *ether*. The solutions have an alkaline reaction.

¶ *Amidogen-nucleus* $C^{14}Ad^2H^4$.

## Biamidobenzoic Acid.

$C^{14}NH^8O^4 = C^{14}Ad^2H^4,O^4$.

VOIT. *Ann. Pharm.* 99, 106; *Chem. Soc. Qu. J.* 9, 271.

*Formation and Preparation.* By the action of hydrosulphate of ammonia on binitrobenzoic acid (p. 135). Sulphuretted hydrogen is passed for some time through a hot ammoniacal solution of binitrobenzoic acid; the solution filtered from sulphur, evaporated over the water-bath, supersaturated with hydrochloric acid and filtered hot; the crystals of hydrochlorate of biamidobenzoic acid which separate on cooling, converted into sulphate by digestion in sulphuric acid; and the sulphate decomposed by carbonate of baryta. The filtrate, which contains the free biamidobenzoic acid, is then evaporated, first over the water-bath and then over oil of vitriol.

*Properties.* Small greenish acuminated crystals, tasteless and without action on vegetable colours; they melt and blacken at about 195°, and cannot be sublimed.

*Decompositions.* Biamidobenzoic acid heated to 100° in a sealed tube with iodide of ethyl, becomes solid; but on adding hydrochloric acid to the aqueous solution of the solid mass, white needles are obtained consisting merely of hydrochlorate of biamidobenzoic acid; no biamidobenzoic ether appears to be formed. — Nitrous acid vapour passed for several days into a hot aqueous solution of biamidobenzoic acid, forms a red resinous, uncrystallisable mass, which has not been further examined.

*Combinations.* The acid dissolves readily in *water*. — Though called an acid, it exhibits rather basic than acid properties; for it does not combine with bases, but forms crystallisable compounds with acids. It will be observed that amidobenzoic acid, formed from benzoic acid by the substitution of 1 At. $NH^2$ for H, exhibits basic as well as acid properties, while in biamidobenzoic acid, in which 2H are thus replaced by 2 At. $NH^2$, the basic character is still more marked.

*Sulphate of Biamidobenzoic acid.* — When the hydrochlorate is dissolved in dilute sulphuric acid and the solution concentrated, brownish tables and laminæ are deposited, which may be obtained nearly colourless

by crystallisation from alcohol. They dissolve readily in water, somewhat less in alcohol; the solutions decompose very easily, and appear brownish yellow by transmitted, grass-green by reflected light.

| | *Dried over oil of vitriol.* | | | Volt. |
|---|---|---|---|---|
| 14 C | 84 | 33·60 | 34·33 | 33·55 |
| 10 H | 10 | 4·00 | 4·65 | 4·93 |
| 2 N | 28 | 11·20 | 11·29 | 10·94 |
| 6 O | 48 | 19·20 | 17·48 | 17·90 |
| 2 $SO^3$ | 80 | 32·00 | 32·25 | 32·68 |
| $C^{14}Ad^2H^4O^4,2SO^4H$ | 250 | 100·00 | 100·00 | 100·00 |

*Hydrochlorate.* — The impure compound prepared in the manner already described may be purified by dissolving it in a small quantity of water and adding strong hydrochloric acid, whereupon either white needles are immediately deposited, or a flocculent precipitate is formed which afterwards changes to the same needles: if these are not quite pure, the operation must be repeated. — The compound dissolves very easily in water, alcohol and ether; the aqueous solution decomposes on exposure to the air, depositing black flocks. The dry compound melts when heated, then decomposes, and yields a sublimate of sal-ammoniac.

| | *At* 60°. | | Volt. |
|---|---|---|---|
| $C^{14}N^2H^8O^4$ | 152·0 | 67·76 | |
| 2 HCl | 72·4 | 32·24 | 31·83 |
| $C^{14}Ad^2H^4O^4,2HCl$ | 224·4 | 100·00 | |

The salt for analysis was pressed between paper and dried, first over oil of vitriol, then at 60°.

*Chloroplatinate.* $C^{14}Ad^2H^4O^4,2HCl,PtCl^2$. — The aqueous solution of the hydrochlorate is not precipitated by bichloride of platinum, even on addition of alcohol and ether; but the mixture, when left to evaporate over oil of vitriol, deposits brown crusts which yield a greyish white powder, and when ignited leave 24·8 p.c. platinum, agreeing nearly with the above formula, which requires 25·01 p.c.

*Nitrate.* — Obtained by decomposing the sulphate with nitrate of baryta; separates in dark-coloured crystals.

*Acetate.* — Prepared by precipitating the sulphate with acetate of baryta. The solution decomposed during evaporation and deposited a brown powder; but by further evaporating the filtered liquid, brownish prisms were obtained.

*Oxalate.* — Brown needles, obtained by evaporating the solution of the hydrochlorate with oxalic acid.

## Sulphobenzamide.

$C^{14}N^2H^6S^2O^6 = C^{14}Ad^2H^4,2SO^2$.

LIMPRICHT & v. USLAR. *Ann. Pharm.* 102, 253.

*Sulphate of Biamidobenzylene, Nitride of Sulphobenzoyl and Hydrogen, Biamide of Sulphobenzoyl.*

Produced by the action of ammonia on chlorosulphobenzoic acid (p. 118).

$$C^{14}H^4S^2O^6,Cl^2 + 2NH^3 = C^{14}H^4S^2O^6,N^2H^4 + 2HCl.$$

Strong aqueous ammonia is added by small portions to chlorosulphobenzoic acid, till no further evolution of heat can be observed; the precipitate washed with a small quantity of cold water to remove sal-ammoniac; and the residual amide purified by crystallisation from hot alcohol, with addition of animal charcoal. If the precipitate be previously dried and absolute alcohol be used to dissolve it, the crystals obtained are perfectly anhydrous; but if hydrated alcohol is used, the crystals which separate consist partly of the anhydrous amide and partly of a hydrate containing 2 At. water.

Anhydrous sulphobenzamide forms small crystals having a glassy lustre; the hydrate crystallises in small needles, which give off from 7·8 to 8·9 p. c. (2 At.) water at 100°, but not over oil of vitriol at ordinary temperatures. The amide melts at 170°, remains soft for a long time after cooling, and ultimately solidifies in a vitreous fissured mass. It remains unaltered at 230°, and exhibits but slight decomposition between 270° and 290°. Even when it is kept for a long time at that temperature, no sulphobenzamide appears to form; indeed the only well characterised substance found in the residue was sulphobenzoamide itself.

| *Anhydrous.* | | | Limpricht & v. Uslar. |
|---|---|---|---|
| 14 C | 84 | 42 | 42·3 |
| 2 N | 28 | 14 | 14·2 |
| 8 H | 8 | 4 | 4·5 |
| 2 S | 32 | 16 | 16·3 |
| 6 O | 48 | 24 | 22·7 |
| $C^{14}N^2H^8S^2O^6$ | 200 | 100 | 100·0 |

| *Hydrated.* | | | Limpricht & v. Uslar. |
|---|---|---|---|
| 14 C | 84 | 38·5 | 37·8 |
| 2 N | 28 | 12·8 | 12·5 |
| 10 H | 10 | 4·6 | 5·1 |
| 2 S | 32 | 14·7 | |
| 8 O | 64 | 29·4 | |
| $C^{14}N^2H^8S^2O^6 + 2Aq$ | 218 | 100·0 | |

The compound may be regarded as *biamide of sulphobenzoyl* = $(NH^2)^2,C^{14}H^4(S^2O^4)O^2$, or nitride of sulphobenzoyl and hydrogen = $N^2\left\{\begin{matrix}C^{14}H^4(S^2O^4)O^2\\H^2\\H^2\end{matrix}\right.$

Sulphobenzamide is nearly insoluble in cold, but easily soluble in hot *water;* in cold *alcohol* it dissolves sparingly, in hot alcohol readily.

¶. *Amidochloro-nucleus* $C^{14}ClAdH^4$.

## Chlorobenzamide.

$$C^{14}NH^6ClO^2 = C^{14}ClAdH^4,O^2.$$

LIMPRICHT & V. USLAR. *Ann. Pharm.* 102, 263.

Chloride of chlorobenzoyl (p. 116) dissolves with great evolution of heat in concentrated aqueous ammonia, and the solution deposits yellow laminated crystals of chlorobenzamide which may be purified by recrystallisation from hot water or alcohol. They melt at 122°, and sublime in small quantity at the same temperature.

| | | | Limpricht & v. Uslar. |
|---|---|---|---|
| 14 C | 84·0 | 53·8 | 54·5 |
| N | 14·0 | 9·0 | 8·7 |
| 6 H | 6·0 | 3·9 | 4·4 |
| Cl | 35·4 | 23·0 | |
| 2 O | 16·0 | 10·3 | |
| $C^{14}NH^5ClO^2$ | 145·4 | 100·0 | |

= Nitride of chlorobenzoyl and hydrogen $N\left\{\begin{matrix} C^{14}H^4ClO^2 \\ H \\ H \end{matrix}\right.$

Chlorobenzamide is sparingly soluble in cold *water*, but dissolves readily in hot water and in *alcohol*. (Limpricht & v. Uslar.) ¶.

*Amidonitro-nucleus* $C^{14}AdXH^4$.

## Nitrobenzamide.

$C^{14}N^2H^6O^6 = C^{14}AdXH^4,O^2$.

FIELD. *Ann. Pharm.* 65, 54.
CHANCEL. *Compt. chim.* 1849, 180; *J. pr. Chem.* 47, 148.

*Formation and Preparation.* 1. Nitrobenzoate of ammonia kept for some time in the state of fusion, yields a substance which is insoluble in cold water, but may be recrystallised from hot water. (Field.)—The preparation is not always successful, as the nitrobenzoate of ammonia sometimes explodes. (Field.)—2. Nitrobenzoate of ethyl is dissolved in a rather large quantity of alcohol, the solution mixed with as much aqueous ammonia as can be added without precipitating the ether, and the mixture left to stand in close vessels (for 8 or 10 days at a gentle heat, for a longer time at ordinary temperatures) till a sample of the liquid no longer becomes turbid on addition of water. The liquid is then evaporated over the water-bath till it crystallises on cooling, and the nitrobenzamide is obtained pure by two or three crystallizations from a mixture of ether and alcohol. (Chancel.)

*Properties.* Nitrobenzamide crystallises from water in yellow needles (Field); by evaporation from solution in wood-spirit, alcohol or ether, in long needles, or by very slow evaporation in tabular crystals resembling gypsum, derived from a rhombic prism. It melts at a temperature above 100°, and solidifies in the crystalline form on cooling. (Chancel.)

| | | | Field. | Chancel. |
|---|---|---|---|---|
| 14 C | 84 | 50·60 | 50·39 | 50·50 |
| 2 N | 28 | 16·87 | | 16·90 |
| 6 H | 6 | 3·61 | 3·98 | 3·75 |
| 6 O | 48 | 28·92 | | 28·85 |
| $C^{14}N^2H^6O^6$ | 166 | 100·00 | | 100·00 |

*Decompositions.* 1. Nitrobenzamide heated with aqueous potash forms nitrobenzoate of potash. (Chancel.) — 2. The alcoholic solution is decomposed by hydrosulphate of ammonia in a very complicated manner; but the aqueous solution yields sulphur and aniline-urea* (isomeric with *carbanilamide*, $C^{14}N^2H^8O^2$).

$$C^{14}N^2H^6O^6 + 6HS = C^{14}N^2H^8O^2 + 4HO + 6S. \text{ (Chancel.)}$$

Nitrobenzamide dissolves sparingly in cold, easily in hot *water*; easily in *wood-spirit*, *alcohol* or *ether*. (Chancel.)

¶ *Amidonitro-nucleus* $C^{14}AdX^2H^3$.

## Binitrobenzamide.

$$C^{14}N^3H^5O^{10} = C^{14}AdX^2H^3,O^2.$$

VOIT. *Ann. Pharm.* 99, 105.

Binitrobenzoate of ethyl (p. 136) digested for several days with alcoholic ammonia, dissolves and forms a blood-red liquid which after concentration, deposits binitrobenzamide in prisms and laminæ having a faint yellowish colour and fatty lustre.

The compound dissolves sparingly in cold, more readily in hot water, forming a solution which has a bitter taste and is neutral to vegetable colours. It melts at 183°, and decomposes at a higher temperature without subliming. The ammoniacal solution does not precipitate nitrate of silver.

| | | | Voit. |
|---|---|---|---|
| 14 C | 84 | 39·81 | 40·87 |
| 5 H | 5 | 2·37 | 2·88 |
| N | 14 | 6·63 | 6·90 |
| 2 $NO^4$ | 92 | 43·60 | |
| 2 O | 16 | 7·59 | |
| $C^{14}AdX^2H^3,O^2$ | 211 | 100·00 | |

May be regarded as *nitride of binitrobenzoyl* and *hydrogen*= $N\left\{\begin{matrix} C^{14}H^3X^2O^2 \\ H \\ H \end{matrix}\right.$ ¶.

* The name aniline-urea does not, strictly speaking belong to the compound $C^{14}N^2H^8O^2$, described at page 303, vol. xi, inasmuch as that compound does not combine with acids; whereas the isomeric body produced by the action of hydrosulphate of ammonia on nitrobenzamide, does combine with acids, and may be regarded as urea in which 1 At. H is replaced by phenyl [$C^{14}N^2H^8O^2 = C^2N^2(C^{12}H^5)H^3O^2$]. (Chancel. *Compt. chim.* 1849, 182.)

*Conjugated Amides of the Benzylene Series.*

## Benzoyl-urea.

$C^{16}N^2H^8O^4 = C^2Ad(N.H,C^{14}H^5O^2),O^2$.

ZININ. (1854.) *Bullet. Petersb.* 12, 281.

***Benzoylharnstoff, Benzureid.***

*Formation.* By heating chloride of benzoyl with urea:

$$C^2Ad(NH^2)O^2 + C^{14}H^5O^2,Cl = C^2Ad(NH,C^{14}H^5O^2)O^2 + HCl.$$

*Preparation.* 6 pts. (2 At.) of dry and pulverised urea (the quantity not exceeding 12 to 16 grammes) are heated with 7 pts. (1 At.) of chloride of benzoyl in the oil-bath to 150—155°; the vessel removed from the bath as soon as the urea is completely melted, and the mixture well stirred, whereupon it becomes hot, and coagulates into a soft kneadable mass, which may be rubbed to small lumps when the action is over, and becomes tolerably hard when cold. The action is not attended with any decrease of weight. — If the temperature rises above 160°, a faint odour of benzonitrile becomes perceptible. — On washing the mass with cold alcohol, which takes up hydrochloric acid and urea [hydrochlorate of urea? L.], benzoyl-urea remains in the form of a crystalline powder, which may be recrystallised from boiling alcohol.

*Properties.* Colourless, highly lustrous, long, thin, four-sided, often acuminated laminæ, united in broad groups.

| | | | | Zinin. |
|---|---|---|---|---|
| 16 C | 96 | 58·53 | | 58·68 |
| 2 N | 28 | 17·07 | | 16·38 |
| 8 H | 8 | 4·87 | | 4·97 |
| 4 O | 32 | 19·53 | | 19·97 |
| $C^{16}N^2H^8O^4$ | 164 | 100·00 | | 100·00 |

Melts at about 200°, and forms on cooling a crystalline mass, which is more soluble in water than the original substance and crystallises in a different form. When the heat is raised some degrees above the melting point, the liquid begins to froth, and suddenly becomes filled with long white needles of cyanuric acid; from the cooled mass, alcohol extracts benzamide:

$$3C^{16}N^2H^8O^4 = C^6N^3H^3O^6 + 3C^{14}NH^7O^2.$$

Benzoyl-urea heated on platinum-foil melts, gives off an odour of benzonitrile, and volatilises completely, the odour of cyanic acid becoming perceptible at the last. — It is decomposed when heated with *nitric acid*, and the solution on cooling yields crystals of benzoic acid. — Boiled with *potash-ley*, it gives off ammonia, and yields benzoate and carbonate of potash.

It dissolves sparingly in *water*, even at the boiling heat, more easily in hot and rather strong *hydrochloric-acid*, and crystallises out in its

original state on cooling. It dissolves readily in cold *potash-ley*, and is precipitated therefrom by acids without alteration, even if the solution has been gently heated. — It is not attacked by *ammonia*. — It dissolves in 100 parts of cold *alcohol*, in 24 pts. of boiling alcohol, and in smaller proportion in *ether*.

## Benzanilide.

$C^{26}NH^{11}O^2 = C^{14}(N.H,C^{12}H^5)H^5,O^2$ or $C^{12}(NH,C^{14}H^5O^2)H^5$.

GERHARDT. (1845.) *Compt. rend.* 20, 1038; also *N. Ann. Chim. Phys.* 14, 124; *N. J. Pharm.* 8, 60.—*N. J. Pharm.* 9, 412; abstr. *J. pr. Chem.* 38, 304.—*N. Ann. Chim. Phys.* 37, 327; also *Ann. Pharm.* 87, 164.

*Phänylbenzamid, Benzoylphänylamid, Azoture de phényle, de benzoïle et d'hydrogène.*

*Formation and Preparation.* When benzoic anhydride is dissolved in heated aniline, a formation of water is observed. A slight excess of aniline is used, and the product is washed with water containing a little hydrochloric acid, and crystallised from boiling alcohol. — 2. When chloride of benzoyl which has been rectified over chloride of calcium is dropped upon aniline, great heat is evolved and a crystalline mass is produced. This mass is exhausted with boiling water, washed with water slightly alkaline to remove any accidental traces of benzoic acid, and crystallised from alcohol. If the crystals are still coloured, they may be purified by careful distillation.

*Properties.* Crystallises from the alcoholic solution by spontaneous evaporation in laminæ having a pearly lustre. Melts when heated, and yields on boiling a distillate which solidifies in the crystalline form as it cools.

| | | | | Gerhardt, (1). | (2). |
|---|---|---|---|---|---|
| 26 C | 156 | | 79·19 | 79·98 | 78·7 |
| N | 14 | | 7·11 | | |
| 11 H | 11 | | 5·58 | 5·63 | 5·9 |
| 2 O | 16 | | 8·12 | | |
| $C^{26}NH^{11}O^2$ | 197 | | 100·00 | | |

[= $N,\overbrace{C^{12}H^5,C^{14}H^5O^2,H}$ = nitride of phenyl, benzoyl and hydrogen].

Decomposes when distilled at a strong heat, and yields an oil which does not solidify. — It is not attacked by boiling dilute acids. When fused with hydrate of potash, it gives off aniline and yields benzoate of potash.

It is insoluble in water, but soluble in *alcohol*.

## Bibenzanilide.

$C^{40}NH^{15}O^4 = C^{14}(N.C^{12}H^5,C^{14}H^5O^2)H^5,O^2$ or $C^{12}(N.2C^{14}H^5O^2)H^5$.

GERHARDT & CHIOZZA. (1853.) *Compt. rend.* 37, 90.—*N. Ann. Chim. Phys.* 46, 137.

*Dibenzanilide, Bibenzoylphenylamide, Phenyldibenzamide, Azoture de benzoïle de phényle et de benzoïle.*

When benzamide is heated with chloride of benzoyl to between 160° and 180°, hydrochloric acid is evolved in large quantity:

$$C^{14}(NH,C^{12}H^5)H^5,O^2 + C^{14}H^5O^2,Cl = C^{14}(N,C^{14}H^5O^2,C^{12}H^5)H^5,O^2 + HCl.$$

The mass, which is liquid at first but solidifies on cooling, is digested with carbonate of soda to remove the excess of chloride of benzoyl, and the residue is dissolved in boiling alcohol. The solution on cooling deposits delicate shining needles, sometimes aggregated in granular masses. The compound melts at about 137° and solidifies in a crystalline mass on cooling. At a higher temperature, it sublimes in small tufts.

| | | | Gerhardt & Chiozza. |
|---|---|---|---|
| 40 C | 240 | 79·7 | 79·7 |
| N | 14 | 4·6 | 4·8 |
| 15 H | 15 | 5·0 | 5·1 |
| 4 O | 32 | 10·7 | 10·4 |
| $C^{40}NH^{15}O^4$ | 301 | 100·0 | 100·0 |

$= \overbrace{N,C^{12}H^5,(C^{14}H^5O^2)^2}$, nitride of phenyl and bibenzoyl.

Dissolves sparingly in boiling *water*, and separates on cooling in small perfectly white needles. *Ammonia* dissolves it somewhat more readily, and deposits it in white flakes on cooling. It dissolves easily in absolute *alcohol* and in *ether*.

## Benzosulphophenamide.

$C^{26}NH^{11}S^2O^6 = C^{14}(N.H,C^{12}H^5S^2O^4)H^5,O^2$ or $C^{12}(N.H,C^{14}H^5O^2)H^5S^2O^4$.

GERHARDT & CHIOZZA. (1853). *Compt. rend.* 37, 186; 38, 457; *Gerh. Traité.* 3, 75.—*N. Ann. Chim. Phys.* 46, 145.

When chloride of benzoyl and sulphophenamide are heated together in equal numbers of atoms, hydrochloric acid escapes in large quantity at 120°, and the mixture becomes perfectly fluid. The temperature is maintained between 140° and 145° as long as hydrochloric acid escapes, and the liquid is poured into a basin, where it solidifies in the crystalline state on cooling, the solidification being attended with considerable rise of temperature. It is purified by recrystallisation from boiling alcohol,

after having been freed from any remaining traces of chloride of benzoyl by macerating it in the pulverised state with ether. It is important in the preparation, to keep the temperature within the limits above mentioned, and not to act on too great quantities at a time, as otherwise a secondary action takes place, attended with formation of benzonitrile and phenylsulphurous acid.

Crystallises from boiling alcohol, in beautiful needles or interlaced prisms, colourless, shining and truncated. Melts between 135° and 140°, and solidifies in a crystalline mass between 130° and 120°. When quickly heated in a tube, it burns and gives off vapours of benzonitrile, and no longer solidifies on cooling.

| | | | Gerhardt & Chiozza. |
|---|---|---|---|
| 26 C | 156 | 59·8 | 60·1 |
| N | 14 | 5·4 | 5·6 |
| 11 H | 11 | 4·2 | 4·3 |
| 2 S | 32 | 12·2 | 12·4 |
| 6 O | 48 | 18·4 | 17·6 |
| $C^{26}NH^{11}S^2O^6$ | 261 | 100·0 | 100·0 |

$= \overbrace{N,C^{12}H^5S^2O^4,C^{14}H^5O^2}$,H, nitride of sulphophenyl, benzoyl, and hydrogen.

The compound has an acid reaction and dissolves readily in alkalis. — Ammonia converts it into benzosulphophenylamic acid.

It dissolves very sparingly in *water*, somewhat more readily in *ether*, readily in absolute *alcohol*.

*Silver-salt.* — When a boiling solution of nitrate of silver is added to a boiling ammoniacal solution of benzosulphophenylamide, and the liquid is kept boiling for a few minutes, and then filtered, the silver salt separates on cooling in beautiful colourless needles, sometimes aggregated in hemispherical groups.

| | | | Gerhardt & Chiozza. |
|---|---|---|---|
| 26 C | 156 | 42·3 | 42·2 |
| N | 14 | 3·8 | 3·6 |
| 10 H | 10 | 2·7 | 3·0 |
| Ag | 108 | 29·3 | 29·8 |
| 2 S | 32 | 8·7 | |
| 6 O | 48 | 13·2 | |
| $C^{26}NH^{10}AgS^2O^6$ | 368 | 100·0 | |

$= \overbrace{N,C^{14}H^5S^2O^4,C^{14}H^5O^2}$,Ag, nitride of sulphophenyl, benzoyl and silver, or benzosulphophenargentamide.

Heated over a spirit lamp, it decomposes quietly, giving off sulphurous acid and benzonitrile, and leaving a black residue of metallic silver mixed with charcoal.

It dissolves but very sparingly in cold water, more readily in boiling water; boiling alcohol dissolves it with tolerable facility.

*Ammonio-silver-salt.* $NH^3,C^{26}N\,H^{10}AgS^2O^6$. — When a solution of the preceding salt in a small quantity of strong ammonia, is left to evaporate, this compound is deposited in splendid crystals having a faint rose-colour, apparently belonging to the oblique prismatic system, and approximating to the form of a prism with rectangular base, modified on

the edges parallel to the vertical axis, and having their summits truncated by two faces parallel to the longer diagonal. When heated, they swell up and decompose, giving off ammonia. They dissolve readily in boiling water, and if the solution be boiled for some time, ammonia is given off, and on cooling two kinds of crystals are obtained, viz., needles of benzosulphophenargentamide, and prisms of the unaltered ammonio-compound. — The aqueous solution mixed with nitric acid, becomes turbid and deposits, on agitation, white flakes of benzosulphophenamide.

| | | | Gerhardt & Chiozza. |
|---|---|---|---|
| 26 C | 156 | 40·5 | 40·5 |
| 2 N | 28 | 7·3 | 7·5 |
| 13 H | 13 | 3·4 | 3·7 |
| Ag | 108 | 28·0 | |
| 2 S | 32 | 8·3 | |
| 6 O | 48 | 12·5 | |
| $NH^3,C^{26}NH^{10}AgS^2O^6$ | 385 | 100·0 | |

= binitride of sulphophenyl, benzoyl, silver and hydrogen— $N^3,\overbrace{(C^{12}H^5S^2O^4),(C^{14}H^5O^2),Ag,H^2}$, or nitride of sulphophenyl, benzoyl and argentammonium, $N,\overbrace{(C^{12}H^5S^2O^4),(C^{14}H^5O^2),(NH^3Ag)}$.

## ¶. Sulphophenylbenzamic Acid.

$C^{26}NH^{13}S^2O^6 = C^{14}(N.H,C^{12}H^5S^2O^4)H^5O^2,H^2O^2$.

GERHARDT & CHIOZZA. *N. Ann. Chim. Phys.* 46, 147.

Obtained by dissolving benzosulphophenamide in aqueous ammonia. The solution evaporated at a gentle heat, or better in vacuo, yields the acid ammonia-salt of sulphophenylobenzamic acid in the form of a thick syrup which ultimately solidifies in a radiated mass.

| *Acid Ammonia-salt.* | | | Gerhardt & Chiozza. |
|---|---|---|---|
| 52 C | 312 | 54·3 | 54·6 |
| 3 N | 42 | 6·9 | 6·7 |
| 29 H | 29 | 5·0 | 5·0 |
| 4 S | 64 | 11·3 | |
| 16 O | 128 | 22·5 | |
| $C^{26}N(H^{12},NH^4)S^2O^6 + C^{26}NH^{13}S^2O^6$ | 575 | 100·0 | |

$$= \left.\begin{matrix} N,\overbrace{C^{12}H^5S^2O^4,C^{14}H^5O^2,H^2} \\ NH^4 \end{matrix}\right\}O^2 + \left.\begin{matrix} N,\overbrace{C^{12}H^5S^2O^4,C^{14}H^5O^2,H^2} \\ H \end{matrix}\right\}O^2.$$

The acid ammonia-salt is very soluble in water and alcohol but insoluble in ether. On adding an acid to the aqueous solution, the liquid becomes turbid and deposits an oil which soon changes into beautiful needles of benzosulphophenamide. — When the radiated ammonia-salt is heated in an oil bath, it melts at 82°, gives off traces of ammonia between 82° and 100°, and a considerable quantity at about 140°, but no

water is deposited on the sides of the tube. The residue is an oily liquid, which when dissolved in alcohol and reprecipitated by water, resembles the substance precipitated by acids from the aqueous solution of the ammonia-salt.

## Benzacetosulphophenamide.

$C^{30}NH^{15}S^2O^8 = C^{14}(N.C^4H^3O^2,C^{12}H^5S^2O^4)H^5O^2$ or

$C^{12}(N.C^4H^3O^2,C^{14}H^5O^2)H^5S^2O^4$ or $C^4(N.C^{12}H^5S^2O^4,C^{14}H^5O^2)H^3O^2$.

*Nitride of Sulphophenyl, Benzoyl and Acetyl,* $N,\overbrace{C^{12}H^5S^2O^4,C^{14}H^5O^2,C^4H^3O^2}$.

Obtained by the action of chloride of acetyl ($C^4H^3O^2,Cl$) on benzosulphophenargentamide. The two substances act upon one another energetically without the aid of heat, and the product treated with boiling ether yields a solution, which when evaporated deposits the compound in small shiaing needles. (Gerhardt & Chiozza, *N. Ann. Chim. Phys.* 46, 150.)

## Bibenzosulphophenamide.

$C^{40}NH^{15}S^2O^8 = C^{14}(N.C^{12}H^5S^2O^4,C^{14}H^5O^2)H^5O^2 = C^{12}(N.2C^{14}H^5O^2)H^5S^2O^4$.

GERHARDT & CHIOZZA. *N. Ann. Chim. Phys.* 46, 155.

*Dibenzoylsulphophenylamide, Azoture de sulfophenyle et de dibenzoïle.*

Obtained by the action of chloride of benzoyl on benzosulphophenargentamide. Chloride of silver is immediately formed, together with a viscid mass which dissolves in ether, forming a solution from which by evaporation, bibenzosulphophenamide is obtained in splendid crystals. [When chloride of benzoyl is brought in contact with benzosulphophenamide, hydrochloric acid is evolved, but the product remains liquid after cooling and contains benzonitrile together with a substance which is transformed by alkalis into benzoic acid and phenylsulphurous acid. This substance is probably $C^{26}H^{10}S^2O^8 = \left.\begin{matrix}C^{14}H^5O^2\\C^{12}H^5S^2O^4\end{matrix}\right\}O^2$; for: $C^{26}NH^{11}S^2O^6 + C^{14}H^5O^2Cl = C^{14}H^5N + C^{26}H^{10}S^2O^8 + HCl$.]

Large, brilliant, truncated prisms, modified with octohedral faces. The substance melts at 105°, and softens even at 100°. After fusion, it retains the viscous state for a long time, and can be recrystallised only by dissolving it in ether. At a high temperature, it decomposes, yielding benzonitrile together with other products.

| | | | | Gerhardt & Chiozza. |
|---|---|---|---|---|
| 40 C | 240 | 65·75 | | 65·79 |
| N | 14 | 3·83 | | 4·12 |
| 15 H | 15 | 4·11 | | 4·36 |
| 2 S | 32 | 8·77 | | 9·02 |
| 8 O | 64 | 17·54 | | 16·71 |
| $C^{40}NH^{15}S^2O^8$ | 365 | 100·00 | | 100·00 |

$= N,\overbrace{C^{12}H^5S^2O^4,(C^{14}H^5O^2)^2}$, nitride of sulphophenyl and bibenzoyl.

The compound is slightly soluble in ammonia. Boiling ether dissolves it but slowly under the ordinary atmospheric pressure, but easily at 100° in a closed tube, and the solution, when left to evaporate, deposits the compound in fine crystals, even with only small quantities of substance.

## Succinylbisulphophenylbibenzamide.

$C^{60}N^2H^{24}S^4O^{16} = C^{28}(N^2.C^8H^4O^4,2C^{12}H^5S^2O^4)H^{10}O^4$ or
$C^8(N.C^{12}H^5S^2O^4,C^{14}H^5O^2)^2H^4O^4$ or $C^{24}(N^2.C^8H^4O^4,2C^{14}H^5O^2)H^{10}S^4O^8$.

GERHARDT & CHIOZZA. *N. Ann. Chim. Phys.* 46, 161; *Compt. rend.* 38, 457; *Gerh. Traité.* 3, 77.

*Diazoture de sulphophényle, de benzoïle, et de succinyle.*

Obtained by heating 2 At. benzosulphophenargentamide (p. 157) with 1 At. chloride of succinyl.

$$2C^{26}NH^{10}AgS^2O^6 + C^8H^4O^4,Cl^2 = 2AgCl + C^{60}N^2H^{24}S^4O^{16}.$$

The resulting mass is exhausted with ether, and the solution when left to evaporate deposits small needles, which are purified by washing with ether. The ethereal solution still retains an oily substance, which ultimately crystallises in needles identical with the preceding.

The compound melts at about 146°. Heated with ether in a closed tube, it dissolves, and the solution yields, by cooling and evaporation, very thin elongated laminæ, radiating from several distinct centres. Under the ordinary pressure, ether dissolves the substance but slowly when crystallised, but readily and in all proportions when in the viscous state.

| | | | Gerhardt & Chiozza. |
|---|---|---|---|
| 60 C | 360 | 59·6 | 59·4 |
| 2 N | 28 | 4·6 | 4·3 |
| 24 H | 24 | 4·0 | 4·4 |
| 4 S | 64 | 10·6 | |
| 16 O | 128 | 21·2 | |
| $C^{60}N^2H^{24}S^4O^{16}$ | 604 | 100·0 | |

$= N^2(C^{12}H^5S^2O^4)^2,(C^{14}H^5O^2)^2,C^8H^6O^4$, nitride of bisulphophenyl, bibenzoyl, and succinyl, the last, $C^8H^6O^4$ being a biatomic radical equivalent to $H^2$.

## T. Sulphobenzanilide.

$C^{38}N^2H^{16}S^2O^6 = C^{14}(N^2,H^2,C^{12}H^5,C^{12}H^5S^2O^4)H^4,O^2 = C^{14}Ad^2(^{12}H^5)H^2.2SO^3$.

LIMPRICHT & v. USLAR. *Ann. Pharm.* 102, 258.

*Sulphobenzobiphenylamide, Binitride of Sulphobenzoyl, phenyl, and hydrogen.*

Produced by the action of chlorosulphobenzoic acid (p. 117) on aniline. The solid product after being washed with water, is purified by crystallising several times from alcohol, with addition of animal charcoal.

Small white crystals, which become slightly brown on drying. They melt when heated, and decompose at a higher temperature, with separation of aniline. They are not decomposed by cold potash-ley.

| | | | Limpricht & v. Uslar. |
|---|---|---|---|
| 38 C | 228 | 64·8 | 65·5 |
| 2 N | 28 | 8·0 | |
| 16 H | 16 | 4·5 | 5·2 |
| 2 S | 32 | 9·1 | 8·4 |
| 6 O | 48 | 13·6 | |
| $C^{38}N^2H^{16}S^2O^6$ | 352 | 100·0 | |

$= N^2,(C^{12}H^5)^2,C^{14}H^4S^2O^6,H^2$, or 2 At. ammonia in which 2 atoms of hydrogen are replaced by 2 At. phenyl, and two more by 1 At. of the bisatomic radical sulphobenzoyl $C^{14}H^4S^2O^6$.

The difference between the analytical and calculated results is due to partial decomposition of the crystals.

The compound dissolves sparingly in hot *water;* but readily in hot *alcohol* and *ether.* ¶.

*Azo-nucleus* $C^{14}NH^5$.

## Benzonitrile. $C^{14}NH^5$.

FEHLING. (1844.) *Ann. Pharm.* 49, 91.
LIMPRICHT & V. USLAR. *Ann. Pharm.* 88, 133; also *J. pr. Chem.* 61, 511.

*Cyanide of Phenyl, Stickstoffbenzen, Stickstoffbenzoyl.*

*Formation.* 1. By the dry distillation of benzoate of ammonia. (Fehling, Laurent & Chancel.) — 2. By the dry distillation of hippuric acid (Limpricht & v. Uslar,) or by distilling hippuric acid with quartz-sand and dry chloride of zinc. (Gössman.) — 3. By treating benzoate of ammonia with dilute sulphuric acid. (Dumas, *Compt. rend.* 25, 384.) — 4. By the action of pentachloride of phosphorus on benzamide. (Cahours.) — 5. By the action of benzoic anhydride or chloride of benzoyl on benzamide (p. 141). — ¶. 6. By heating benzamide with anhydrous phosphoric acid. (Buckton & Hofmann, *Chem. Soc. Qu. J.* 9, 255.) — 6. By the action of chloride of benzoyl on sulphocyanide of potassium. (Hugo Schiff, *Ann. Pharm.* 99, 117.)

$$C^{14}H^5O^2Cl + C^2NKS^2 = C^{14}NH^5 + KCl + CO^2 + CS^2.$$

7. By heating chloride of benzoyl with cyanate of potash:

$$C^{14}H^5O^2Cl + C^2NKO^2 = C^{14}NH^5 + KCl + 2CO^2.$$

After the action has been continued for some hours, the mixture forms a brown pasty mass, which solidifies on cooling and yields benzonitrile when exhausted with ether. (Schiff, *Ann. Pharm.* 101, 93.) — 8. By heating

benzoic anhydride with cyanate of potash or sulphocyanide of potassium (Schiff):

$$C^{14}H^5O^2 + C^2NK\left\{\begin{matrix}O^2\\ \text{or } S^2\end{matrix}\right. = C^{14}NH^5 + KO,CO^2 + \left\{\begin{matrix}CO^2\\ \text{or } CS^2\end{matrix}\right. \P.$$

Benzonitrile is not produced by heating sulphophenylate of baryta with cyanide of potassium. (Hofmann, *Ann. Pharm.* 74, 32.)

*Preparation.* 1. The solution of benzoic acid in ammonia is evaporated to dryness and heated in a retort; ammonia then escapes, a sublimate forms in the neck of the retort, and water passes over together with a small quantity of oily benzonitrile, the larger quantity however remaining in the retort. The fused residue is therefore covered with water (to which a little ammonia may be added) and distilled to dryness, and these operations are repeated as long as any drops of oil pass over with the water. By this process, 12 oz. of benzoic acid yield in five days 6 oz. of impure benzonitrile. This product is washed with dilute hydrochloric or sulphuric acid and afterwards with water, then dried over chloride of calcium, and rectified. (Fehling.) Buckton & Hofmann, by distilling benzoate of ammonia with chloride of zinc, and rectifying the distillate, obtained a product, only one-third of which consisted of benzonitrile, the remaining two-thirds being benzol. — 2. The distillate obtained by heating hippuric acid to 240° (p. 73) is distilled with water, and the benzonitrile which passes over is rectified over lime. (Limpricht & v. Uslar.) — ¶. 3. When 1 pt. of dry hippuric acid is mixed in a warm mortar with an equal bulk of quartz-sand and 2 pts. of solid chloride of zinc dried as completely as possible, and the mixture heated in a dry retort to about 300°, benzonitrile distils over, a small quantity of charcoal is separated, and carbonic acid gas is quietly given off:

$$C^{18}NH^9O^6 - 4HO = C^{14}NH^5 + CO^2 + 3C.$$

30 grammes of hippuric heated in this manner to a temperature not exceeding 350°, with the utmost possible exclusion of moisture, yielded between 10 and 12 grms. of benzonitrile; a small portion only was resolved into benzoic acid and glycocol [possibly from the presence of a trace of moisture, (p. 74)] and from the decomposition of the latter a small quantity of sal-ammoniac was produced. (Gössmann, *Ann. Pharm.* 100, 69.) — 4. When 1 At. chloride of benzoyl is mixed with 1 At. sulphocyanide of potassium, great heat is produced; the odour of bisulphide of carbon becomes perceptible; and on distilling the product, a slightly coloured liquid passes over, which, after a few rectifications becomes colourless, and exhibits the characters of benzonitrile. It is probable that sulphocyanide of benzoyl is first produced and afterwards resolved into benzonitrile, carbonic acid and bisulphide of carbon (Schiff):

$$C^{14}H^5O^2,C^2NS^2 = C^{14}NH^5 + CO^2 + CS^2.$$

5. According to Buckton & Hofmann, the best, though a tedious process for preparing benzonitrile, is to distil benzamide with anhydrous phosphoric acid. ¶.

*Properties.* Transparent, colourless, strongly refracting oil (refracting power = 1·503, according to Reusch), having an odour very much like that of bitter almond oil, and a burning taste. (Fehling, Limpricht & v. Uslar.) Sp. gr. = 1·0073; sinks in cold water, but rises to the surface when heated. (Fehling.) Sp. gr. 1·0084 at 16·8, or 1·0230 at 0°.

(H. Kopp, *Ann. Pharm.* 98, 373.) Boils at 191° (Fehling, Schiff); at 192 (Limpricht & v. Uslar); at 190·6°, with the barometer at 733·4 mm. (Kopp.) Vapour-density = 3·7. (Fehling.)

| | | | Fehling. | Chodnew. | Limpricht & v. Uslar. | Schiff. |
|---|---|---|---|---|---|---|
| 14 C | 84 | 81·55 | 81·19 | 80·87 | 81·11 | 81·0 |
| N | 14 | 13·59 | 13·35 | 13·62 | 12·42 | 13 4 |
| 5 H | 5 | 4·86 | 5·16 | 4·97 | 4·99 | 5·1 |
| $C^{14}NH^5$ | 103 | 100·00 | 99·70 | 99·46 | 98·52 | 99·5 |

| | Vol. | Density. |
|---|---|---|
| C-vapour | 14 | 5·8240 |
| N-gas | 1 | 0·9706 |
| H-gas | 5 | 0·3465 |
| Vapour of Benzonitrile | 2 | 7·1411 |
| | 1 | 3·5705 |

*Decompositions.* 1. Benzonitrile burns with a bright sooty flame.— 2. With the stronger *acids* it yields benzoate of ammonia, water being decomposed at the same time. — 3. With strong *sulphuric acid*, it yields sulphobenzoic and bisulphobenzolic acids, bisulphate of ammonia being formed at the same time and carbonic acid evolved. (Buckton & Hofmann, xi. 156; xii. 53.)

$$[2C^{14}NH^5 + 10SO^4H + 2HO = C^{14}H^6S^2O^{10} + C^{12}H^6S^4O^{12} + 2(NH^4,H,2SO^4) + 2CO^2.]$$

4. With hydrosulphate of ammonia, it forms sulphobenzamide. (Cahours.) — 4. Potassium does not act upon it in the cold, but the liquid assumes a brownish colour when heated. (Fehling.) No gas is evolved in this reaction, and no cyanide of potassium is formed. (Dumas, Malaguti & Leblanc, *Compt. rend.* 25, 475.) — Heated with potassium in a sealed tube, it acquires a fine carmine colour, and at 240° yields needle-shaped crystals: water extracts cyanide of potassium from the product; and the residue yields by distillation a green oil smelling like creosote, in which the crystals again form and may be purified by treatment with alcohol and ether, and by sublimation. (Bingley, *Chem. Gaz.* 1854, 329.)

Benzonitrile dissolves in 100 pts. of water at 100°, and separates out again on cooling. With *alcohol* and *ether* it mixes in all proportions.

*Appendix.*

## Sulphocyanobenzylene.

$C^{16}NH^6S^2 = C^{14}H^5,C^2NS^2$. ?

QUADRAT. *Ann. Pharm.* 71, 13.

*Sulphocyanide of Benzoyl.* [This appellation is however incorrect, the term benzoyl denoting $C^{14}H^5O^2$, not $C^{14}H^5$.]

When bitter almond oil, either pure or crude, is mixed with ammonia and bisulphide of carbon, two layers are formed, the upper of which

exhibits a red tint gradually increasing in intensity from the surface of contact with the lower, and deposits a yellow resinous body; when mixed with acids, it gives off sulphuretted hydrogen and deposits a yellow resinous body soluble in potash. The lower layer gradually becomes milky and deposits crystals which disappear again after longer standing, but may be obtained pure by draining off the mother-liquor, pressing between bibulous paper, and washing with ether. — Colourless prisms or granules having a bitter taste.

| | | | Quadrat. |
|---|---|---|---|
| 16 C | 156 | 65·30 | 65·12 |
| N | 14 | 9·52 | 9·40 |
| 5 H | 5 | 3·40 | 3·87 |
| 2 S | 32 | 21·78 | 21·61 |
| $C^{16}NH^{5}S^{2}$ | 207 | 100·00 | 100·00 |

*Decompositions.* 1. When exposed to the air for some time, it exhales a peculiar odour and turns yellow. Melts at 100°, with strong intumescence and incipient decomposition. At 120°, it gives off ammonia, bisulphide of carbon and bitter almond oil. At 150, the yellowish frothing mass suddenly becomes changed to a mobile liquid, ceases to froth, and does not begin to boil till heated to between 210° and 220°, a few needles then subliming, simlar to Laurent's benzoylazotide $C^{28}N^{3}H^{10}$. The residue solidifies on cooling to a yellow resinous mass, containing a few needle-shaped crystals which may be extracted by alcohol of 40°. The body insoluble in alcohol behaves very much like Laurent's benzoylazotide; it is however $C^{16}NH^{5}$ ( = $C^{16}NH^{5}S^{2} - CS^{2}$).

2. Sulphocyanobenzylene boiled with nearly anhydrous *alcohol* gives off hydrosulphate of ammonia and carbonic acid, the liquid acquiring a yellow colour and depositing white laminæ as it cools. The crystals consist of:

| | | | Quadrat. |
|---|---|---|---|
| 56 C | 336 | 71·80 | 71·67 |
| 2 N | 28 | 5·98 | 5·85 |
| 24 H | 24 | 5·13 | 5·23 |
| 5 S | 80 | 17·09 | 17·25 |
| $C^{56}N^{2}H^{24}S^{5}$ | 468 | 100·00 | 100·00 |

Quadrat regards this body as a compound of thiobenzamide with benzosyl ($C^{14}H^{5}$) and sulphur ($C^{56}N^{2}H^{24}S^{5} = 2C^{14}NH^{7}S^{2} + C^{14}H^{5} + S$). [The two sides of this equation do not agree. W.] — Compare Laurent (*Compt. chim.* 1850, 86).

3. When sulphocyanobenzylene is dissolved in hot *alcohol* of 40° containing a little *ammonia*, and water added till permanent turbidity is produced, the liquid on cooling yields a crystalline powder which is insoluble in water, and cannot be purified by crystallisation from alcohol, because it decomposes when dissolved in that liquid.

4. *Ether* likewise dissolves sulphocyanobenzylene with decomposition.

5. Sulphocyanobenzylene imparts to aqueous *sesquichloride of iron*, a blood-red colour, arising from the formation of ferric sulphocyanide; on heating the liquid, bitter almond oil distils over;

$$3C^{16}NH^{5}S^{2} + Fe^{2}Cl^{3} + 6HO = Fe^{2}(CyS^{2})^{3} + 3C^{14}H^{6}O^{2} + 3HCl.$$

## Benzosylanilide.

$C^{26}NH^{11} = C^{14}(C^{12}NH^{6})H^{5} = C^{12}N(C^{14}H^{5})H^{6}$.

LAURENT & GERHARDT. (1850.) *Compt. chim.* 1850, 117; abstr. *Compt. rend.* 30, 405.

*Benzosylanilide.*

*Formation.* By the action of aniline on bitter almond oil:

$$C^{14}H^{6}O^{2} + C^{12}NH^{7} = C^{26}NH^{11} + 2HO.$$

*Preparation.* When a mixture of about equal parts of dried bitter almond oil and aniline, water separates out and rises to the surface; and after a while a crystalline mass more or less coloured is produced. Sometimes the mixture remains liquid, but solidifies when water is poured on it. The mass is pressed and recrystallised from a small quantity of warm alcohol; to render it perfectly colourless, it may also be distilled after pressing; a colourless oil then passes which solidifies in a crystalline mass on cooling.

*Properties.* Beautiful shining crystalline laminæ. Very easily fusible. Distils without decomposition at a high temperature. Inodorous. Tasteless.

| | | | Laurent & Gerhardt. |
|---|---|---|---|
| 26 C | 156 | 86·19 | 85·73 |
| N | 14 | 7·74 | 7·30 |
| 11 H | 11 | 6·07 | 6·97 |
| $C^{26}NH^{11}$ | 181 | 100·00 | 100·00 |

*Decompositions.* 1. Benzosylanilide is immediately decomposed by *bromine,* with great evolution of heat. Bromine acts with violence on the alcoholic solution, and the liquid, after a while, yields crystals of tribromaniline. — 2. With cold fuming *nitric acid,* it forms a dark green solution, from which water throws down bitter almond oil, while nitrate of aniline remains in solution. — 3. With *oil of vitriol* it forms a yellow solution, from which water separates bitter almond oil, while sulphate of aniline remains in solution. — 4. In contact with *hydrochloric acid* it becomes liquid, and is dissolved by the concentrated acid at ordinary temperatures, but appears not to be altered by boiling. — 5. It is scarcely attacked by potash. — 6. *Acetic acid* causes it to liquefy, but does not dissolve it in perceptible quantity.

It is insoluble in water, but dissolves very easily in *alcohol* and in *ether.*

## Flavine. $C^{26}NH^{12}O^{2}$.

LAURENT & CHANCEL. (1848.) *L'Inst.* 1848, 95. — *Compt. chim.* 115, 162; *J. pr. Chem.* 46, 511.
CHANCEL. *Compt. rend.* 28, 85.

*Aniline-urea, Diphenyl-urea.*

*Formation.* By the action of sulphuretted hydrogen on binitrobenzone (p. 86);

$$C^{26}N^{2}H^{8}O^{10} + 12HS = C^{26}N^{2}H^{12}O^{2} + 8HO + 12S.$$

*Preparation.* The product of the dry distillation of benzoate of lime (p. 39), after being freed from benzol and the last portions of the distillate, is boiled for some hours with fuming nitric acid, and the liquid afterwards diluted with water. It then deposits a yellow oil which partly solidifies in the crystalline form on cooling, and after the acid has been poured off, is washed with alcohol and dissolved in a small quantity of ether. The solution solidifies after a few hours, to a crystalline mixture of several bodies difficult to separate from one another; this mixture is dissolved in ether and alcohol, and the liquid filtered. The residue on the filter forms with hydrosulphate of ammonia and ether-alcohol, a solution which, in the course of 24 hours, becomes filled with crystals of flavine. These are collected on a filter and dissolved in hydrochloric acid; the solution filtered to remove the precipitated sulphur and insoluble impurities, then precipitated with ammonia; the precipitate dissolved in hydrochloric acid; and the solution diluted with alcohol and mixed with hydrochloric acid at the boiling heat: it then on cooling deposits slender needles of flavine.

*Properties.* Colourless or pale yellow needles.

| | | | Laurent & Chancel. |
|---|---|---|---|
| 26 C | 156 | 73·57 | 73·1 |
| 2 N | 28 | 13·22 | 13·5 |
| 12 H | 12 | 5·66 | 5·9 |
| 2 O | 16 | 7·55 | 7·5 |
| $C^{26}N^{2}H^{12}O^{2}$ | 212 | 100·00 | 100·0 |

May be regarded as urea in which 2 At. H are replaced by phenyl $C^{4}N^{2}(C^{12}H^{5})^{2}H^{2}O^{2}$. *Comp.* Gerhardt (*Traité* 1, 430.)

When heated with potash, it gives off an oil which has an alkaline reaction and dissolves in acid.

It is almost insoluble in water.

*Hydrochlorate of Flavine.* — *Preparation, vid. sup.* — Long laminæ. By dry distillation, it yields a scanty white sublimate and leaves a very bulky charcoal. — It dissolves very easily in water, somewhat less in alcohol.

*Chloroplatinate of Flavine.* — Obtained as a pulverulent precipitate, on mixing the dilute solutions of bichloride of platinum and hydrochlorate of flavine. After drying at 150°, it contains 31·4 p. c. platinum,

agreeing with the formula $C^{28}N^2H^{12}O^2,2HCl,2PtCl^2$, which requires 31·43 per cent.

Flavine is soluble in *alcohol* and *ether*.

---

*Compounds containing two or more Atoms of $C^{14}H^6$ or of nuclei derived therefrom.**

## Stilbene. $C^{28}H^{12}$.

LAURENT. (1843.) *Compt. rend.* 16, 856.—*Rev. scient.* 16, 373; *J. pr. Chem.* 35, 418.—*Rev. scient.* 18, 201.

The name *stilbene* is derived from στιλβειν to *shine*.

*Formation.* By heating sulphide or nitrosulphide of benzylene. [The resinous substance produced by the action of fluoride of boron, &c., or benzylic alcohol (p. 46), is probably stilbene.]

*Preparation.* 1. The scales which first pass over during the dry distillation of sulphide of stilbene (p. 168), are dissolved in boiling alcohol; the solution filtered from the undissolved thionessal; the mother-liquor drained from the crystalline laminæ which separate on cooling; these laminæ dissolved in excess of ether; and the solution left to evaporate.—2. When the mixture of picril, stilbene, thionessal and lophine (p 25), obtained by the action of hydrosulphate of ammonia on bitter almond oil, is boiled with ether, and the solution left to cool, stilbene crystallises out first, and may be purified by two or three crystallisations from alcohol and ether.

*Properties.* Colourless, pearly laminæ often joined end to end, or short prisms belong to the oblique prismatic system (oP. ∞P. ∞P∞). Fig. 112, without the *h*-faces; $i : t = 112°$; $i : i = 100°$; $u : u = 53° 30'$; $u : t = 116° 45'$; $t : f = 133° 30'$; $i : f = 66°$. Inodorous; solidifies after tranquil fusion at 110° or sometimes not till cooled to 100°; but if agitated, it solidifies at 118°, forming a scaly crystalline mass. Boils at 292°, and pass over undecomposed. Sp. gr. of the vapour = 8·40 (by another method: 8·2).

| | | | | Laurent. |
|---|---|---|---|---|
| 28 C | 168 | 93·33 | | 93·28 |
| 12 H | 12 | 6·67 | | 6·66 |
| $C^{28}H^{12}$ | 180 | 100·00 | | 99·94 |

| | Vol. | Density. |
|---|---|---|
| C-vapour | 28 | 11·6480 |
| H-gas | 12 | 0·8316 |
| Vapour of stilbene | 2 | 12·4796 |
| | 1 | 6·2398 |
| | ½ | 8·3298 |

Hence, stilbene-vapour is ½-atomic.

* As it is impossible to classify these compounds exactly according to the system adopted in this Handbook, they are arranged partly according to their origin and mode of formation.

*Decompositions.* 1. Stilbene boiled for a short time with *nitric acid* forms a yellow resin, which, after washing and drying, contains 73·4 per cent. of carbon and 4·8 p. c. hydrogen, and therefore consists of nitrostilbene mixed with a small quantity of bitter almond oil. (The formula $C^{28}XH^{11}$ requires 74·66 p. c., C and 4·89 H.) If the boiling with nitric acid be continued for some minutes, a mixture is formed containing a larger proportion of binitrostilbene. Laurent found 67·1 p. c., C and 4·2 H; the formula $C^{28}X^{2}H^{10}$ requires 61·49 p. c. C, and 3·70 H. After a quarter of an hour's boiling, nitrostilbic acid is produced in addition to the yellow resin. — 2. Stilbene is not decomposed by dilute *chromic acid;* but the concentrated acid acts on it with violence, forming bitter almond oil. — 3. With *bromine* it gives off vapours of hydrobromic acid and forms hydrobromate of bromostilbene. — 4. *Chlorine gas* is at first absorbed by fused stilbene, without evolution of hydrochloric acid; if the passage of the chlorine be continued and the temperature raised at the same time, hydrochloric acid escapes, and there is formed a mixture of $\alpha$ and $\beta$ hydrochlorate of chlorostilbene, hydrochlorate of bichlorostilbene and an oily chlorine-compound.

*Combinations.* Stilbene dissolves in strong oil of vitriol; the solution forms a soluble baryta-salt.

It dissolves in ether more readily than in alcohol.

## Sulphide of Stilbene. $C^{28}H^{12}S^{4}$.

LAURENT. (1841.) *N. Ann. Chim. Phys.* 1, 292; *Ann. Pharm.* 38, 320.—*Rev. scient.* 16, 373; *J. pr. Chem.* 35, 418.
ROCHLEDER. *Ann. Pharm.* 37, 346.
CAHOURS. *Compt. rend.* 25, 457.

***Schwefelbenzen, Sulfobenzoylwasserstoff, Hydrure de sulfobenzoïle.***

*Formation.* By the action of hydrosulphate of ammonia on bitter almond oil. (Laurent, Rochleder, p. 25.)

$$2C^{14}H^{6}O^{4} + 4HS = C^{28}H^{12}S^{4} + 4HO.$$

or of sulphuretted hydrogen on hydrobenzamide (Cahours).

$$2C^{4}N^{2}H^{13} + 12HS = 3C^{28}H^{12}S^{4} + 4NH^{3}.$$

*Preparation.* 1. When 1 vol. bitter almond-oil is dissolved in 8 to 10 vol. alcohol, and 1 vol. hydrosulphate of ammonia gradually added, the liquid, after a few minutes deposits a mealy powder consisting of sulphide of stilbene. Or an alcoholic solution of bitter almond oil is heated to the boiling point, and mono- or bihydrosulphate of ammonia added in small quantities: the liquid then after a few seconds deposits a white precipitate, which may be purified by washing with alcohol. The alcoholic solution contains small quantities of hydride of sulphazobenzoyl. The preparation does not always succeed. (Laurent.) — 2. When sulphuretted hydrogen is passed in excess through an alcoholic solution of hydrobenzamide, and the liquid afterwards left at rest, it deposits sulphide of stilbene. (Cahours.)

*Properties.* White powder (Laurent, Rochleder) consisting of microscopic granules (Laurent). Softens between 90° and 95°. When carefully heated to the melting point, it solidifies on cooling into a transparent non-crystalline mass. It is inodorous, but imparts to the fingers a very persistent odour of onions. (Laurent.)

| | | | | Laurent. |
|---|---|---|---|---|
| 28 C | 168 | | 68·89 | 68·71 |
| 12 H | 12 | | 4·92 | 5·21 |
| 4 S | 64 | | 26·19 | 25·86 |
| $C^{28}H^{12}S^4$ | 244 | | 100·00 | 99·78 |

Polymeric with sulphide of benzylene (p. 49). [It is perhaps $C^{42}H^{18}S^6$; at least this formula leads to a simpler expression of its formation from hydrobenzamide: $C^{42}N^3H^{18} + 8HS = C^{42}H^{18}S^6 + 2NH^4S$. (L.)].

*Decompositions.* 1. Heated above its melting point, it turns reddish-yellow, and solidifies in a crystalline mass consisting of decomposition-products. (Laurent, Rochleder.) When kept for some time in a state of fusion, it gives off sulphuretted hydrogen and a small quantity of bisulphide of carbon; and if the heat be considerably raised after the escape of the sulphuretted hydrogen, scales of stilbene sublime at first, and afterwards needles of thionessal (Laurent):

$$2C^{28}H^{12}S^4 = 3HS + 2CS^2 + C^{28}H^{12} + C^{28}H^9S.$$

2. It burns with a very offensive odour, and a bright sooty flame. (Laurent, Rochleder.)—3. Decomposes in contact with heated *nitric acid*, with rapid evolution of red fumes and separation of sulphur. (Rochleder.) Nitric acid acts violently upon it at a gentle heat, forming sulphuric acid and bitter almond oil or benzoic acid. (Laurent.) — 4. It is not attacked by cold *oil of vitriol*, but dissolves on the application of heat, forming a carmine-coloured solution (Laurent, Rochleder), which is decolorised, with separation of flakes by water. [Was benzylic acid formed? (L.)] — 5. With *bromine*, it forms an oily mass, while hydrobromic acid is given off. (Laurent.) — With *iodine* it melts into a brown mass which dissolves with yellow colour in alcohol. (Rochleder.) — 6. When boiled with *hydrochloric acid*, it gives off a small quantity of sulphuretted hydrogen. (Laurent.) — 7. With melting *hydrate of potash*, it forms a red mass, whence thick fumes are evolved, which sublime in fern-like groups of crystals like the products obtained from the compound by dry distillation. (Rochleder.) It is slowly decomposed by alcoholic potash, and water throws down from the solution a reddish oil, which forms with nitric acid a body apparently different from benzoic acid. From the alkaline solution free acids evolved sulphuretted hydrogen. (Laurent.)

Sulphide of stilbene is insoluble in water and in alcohol. (Laurent.) When boiled for some time with hydrated alcohol, it dissolves abundantly, forming a yellow solution which does not yield any deposit on cooling. On boiling it gives off sulphuretted hydrogen.

With *ether* it quickly forms a transparent liquid, which dissolves in small quantity in the excess of ether, and is reconverted into a mealy powder by alcohol. (Laurent.)

## Hydrobromate of Bromostilbene.

$C^{28}H^{12}Br^{3} = C^{28}BrH^{11},HBr.$

LAURENT. *Rev. scient.* 16, 373; *J. pr. Chem.* 35, 424.

*Bromure de stilbène.*

Produced by the action of bromine on stilbene — with evolution of hydrobromic acid — in the form of a white powder, which is insoluble in alcohol and ether, and may be purified by washing with ether.

| | | | | Laurent. |
|---|---|---|---|---|
| 28 C | 168 | 49·41 | | 48·2 |
| 2 Br | 160 | 47·06 | | |
| 12 H | 12 | 3·53 | | 3·3 |
| $C^{28}H^{12}Br^{3}$ | 340 | 100·00 | | |

According to Laurent, the substance analysed doubtless contained hydrobromate of bibromostilbene $C^{28}Br^{2}H^{10},HBr$, a supposition which accounts, not only for the difference between the analytical and calculated results, but also for the evolution of hydrobromic acid which accompanies the formation of the compound.

When heated, it gives off hydrobromic acid and a very small quantity of free bromine.

## Chlorostilbene. $C^{28}ClH^{11}$.

LAURENT. *Rev. scient.* 16, 373; *J. pr. Chem.* 35, 425.

*Chlostilbase.*

Produced by the action of alcoholic potash on hydrochlorate of chlorostilbene, and like the latter, forms two modifications, $\alpha$ and $\beta$.

$\alpha$. Hydrochlorate of chlorostilbene boiled with alcoholic potash, yields chloride of potassium and chlorostilbene $\alpha$, which is precipitated by water as an oil capable of being distilled without decomposition. Soluble in alcohol and ether.

| | | | | Laurent. |
|---|---|---|---|---|
| 28 C | 168·0 | 78·25 | | 77·0 |
| Cl | 35·4 | 16·52 | | |
| 11 H | 11·0 | 5·13 | | 5·3 |
| $C^{28}ClH^{11}$ | 214·4 | 99·90 | | |

$\beta$. When hydrochlorate of chlorostilbene $\beta$ is boiled with alcoholic potash, an oil is produced which distils undecomposed, and has doubtless the same composition as $\alpha$.

*Bromide of Chlorostilbene.* — $C^{28}ClH,Br^{2}$. — $\alpha$. Chlorostilbene $\alpha$ combines directly with bromine, forming a solid body, which is obtained in the crystalline state by solution in boiling ether and spontaneous evapo-

ration. Forms small six-sided prisms with dihedral summits. Dissolves sparingly in alcohol and ether.

*β*. When bromine is poured upon chloride of stilbene *β*, a solid mass is formed; and on dissolving this in boiling ether and leaving the solution to evaporate, indistinct crystals are obtained, which yield by distillation bromine, hydrobromic acid, and compounds which crystallise in needles.

| | | | Laurent. *a.* | *β.* |
|---|---|---|---|---|
| 28 C | 168·0 | 44·87 | 43·5 | 46·30 |
| 2 Br | 160·0 | 42·74 | | |
| Cl | 35·4 | 9·45 | | |
| 11 H | 11·0 | 2·94 | 3·0 | 3·05 |
| $C^{28}Br^{2}ClH^{11}$ | 374·4 | 100·00 | | |

## Hydrochlorate of Chlorostilbene.

$C^{28}H^{12}Cl^{2} = C^{28}H^{11}Cl,HCl.$

LAURENT. (1844.) *Rev. scient.* 16, 373; *J. pr. Chem.* 35, 422.

*Chlorure de stilbène.*

*Formation.* Obtained in two isomeric modifications by the action of chlorine gas on melted stilbene.

*a*. When the product of the action of chlorine gas on melted stilbene (p. 168) is treated with cold ether, *a*-hydrochlorate of chlorostilbene remains undissolved, and by solution in boiling ether and slow spontaneous evaporation of the solution, may be obtained in beautiful crystals belonging to the oblique prismatic system. (P, ∞ P, ∞P∞) *Fig.* 114, without *t*; *a* : *m*=106° 31; *u* : *m*=109°. May be partially volatilised without decomposition, but at a higher temperature yields hydrochloric acid and an oily substance. Boiling alcoholic potash converts it into *a*-chlorostilbene. — It dissolves sparingly in ether, and is quite insoluble in alcohol.

*β*. When the ethereal solution separated from *a* is mixed with alcohol and left to evaporate, it yields eight-sided tables of *β*-hydrochlorate of chlorostilbene and dull lenticular crystals of hydrochlorate of bichlorostilbene, while the oily compound remains in solution. The octagonal tables are picked out and recrystallised from a mixture of ether and alcohol. — Colourless, transparent tables belonging to the right prismatic system and having a faint pearly lustre. Fig. 48, without the narrow face and with the *p*-face predominating. (P, P̆∞, o P̄). *p* : *y* about 103°; *p* : *i* about 112°; *p* : *a* about 110°. Boiled with alcoholic potash it yields *β* chlorosalbene. Dissolves readily in alcohol, and still more in ether.

| | | | Laurent. *a.* | *β.* |
|---|---|---|---|---|
| 28 C | 168·0 | 66·99 | 66·32 | 66·82 |
| 2 Cl | 70·8 | 28·23 | | |
| 12 H | 12·0 | 4·78 | 4·84 | 4·83 |
| $C^{28}Cl^{2}H^{12}$ | 250·8 | 100·00 | | |

## Hydrochlorate of Bichlorostilbene.

$C^{28}Cl^{3}H^{11} = C^{28}Cl^{2}H^{10},ClH$.

LAURENT. *Rev. scientif.* 16, 373.

*Chlorure de chlostilbase.*

*Formation and Preparation.*—vid. *Hydrochlorate of Chlorostilbene β.*

From the mixture of hydrochlorate of chlorostilbene and hydrochlorate of bichlorostilbene, the dull lenticular crystals are picked out and recrystallised from ether-alcohol by spontaneous evaporation; or the mixture is repeatedly crystallised from ether, and the hydrochlorate of bichlorostilbene thereby separated from the β-hydrochlorate of chlorostilbene, which is more soluble in ether. White, opaque, lenticular crystals. Melts at 85°.

| | | | | Laurent. |
|---|---|---|---|---|
| 28 C | 168·0 | | 58·91 | 59·27 |
| 3 Cl | 106·2 | | 37·23 | |
| 11 H | 11·0 | | 3·86 | 3·90 |
| $C^{28}Cl^{3}H^{11}$ | 285·2 | | 100·00 | |

According to Laurent, it is $C^{28}H^{11}Cl,CO^{2}$.

When boiled with alcoholic potash, it yields chloride of potassium and an oil containing chlorine.

Somewhat less soluble in ether than hydrochlorate of chlorostilbene.

## Nitrostilbic Acid.

$C^{28}NH^{11}O^{14} = C^{28}XH^{11},O^{10}$.

LAURENT. *Rev. scient.* 16, 373; *J. pr. Chem.* 35, 428.

*Nitrostilbensäure, Acide nitrostilbique.*

When stilbene is boiled for a quarter of an hour with nitric acid, there is formed, besides the resinous nitro-compound (p. 168), an acid liquid which, when decanted and diluted with water, deposits on cooling a light yellowish crystalline powder. This substance is dissolved out with dilute ammonia, and the acid precipitated from the filtrate by nitric acid, washed and dried.

Yellowish crystalline powder, which melts at a higher temperature than nitrobenzoic acid and sublimes in scales.

| | | | | Laurent. |
|---|---|---|---|---|
| 28 C | 168 | | 55·08 | 54·7 |
| N | 14 | | 4·50 | 4·6 |
| 11 H | 11 | | 3·69 | 4·6 |
| 14 O | 112 | | 36·73 | 36·1 |
| $C^{28}NH^{11}O^{14}$ | 305 | | 100·00 | 100·0 |

Nearly insoluble in water, dissolves more readily in alcohol, still more in ether.

*Nitrostilbate of Silver.* — Obtained by precipitating the ammoniacal solution of the acid with nitrate of silver; contains 41·0 p. c. silver, agreeing with the formula $C^{28}XH^{10}Ag^2O^{10}$, which requires 41·6 p. c.

## Benzoïn. $C^{28}H^{12}O^4$.

ROBIQUET. *Ann. Chim. Phys.* 21, 254; *N. Tr.* 7, 235.
ROBIQUET & BOUTRON CHARLARD. *Ann. Chim. Phys.* 44, 364; 40, 294.
BONASTRE. *J. Pharm.* 16, 519; *N. Tr.* 23, 2, 184.
WÖHLER & LIEBIG. *Ann. Pharm.* 3, 276; *Pogg.* 26, 474.
LAURENT. *Ann. Chim. Phys.* 59, 402; *Ann. Pharm.* 17, 881; *Pogg.* 36, 497.—*Ann. Chim. Phys.* 66, 193.
ZININ. *Ann. Pharm.* 34, 186.
GERHARDT. *Rev. scient.* 10, 371.

*Stearoptene of Bitter Almond Oil, Bittermandelölcampher.*—First correctly examined by WÖHLER & LIEBIG in 1832.

*Formation.* 1. Occurs sometimes together with benzamide in crude bitter almond oil. (Laurent.) — When bitter almond oil containing prussic acid is exposed to the air, it forms, besides benzoic acid, a yellow crystalline substance not possessing acid properties. (Robiquet.) Bonastre, in distilled bitter almond oil with spring-water, found in the residue, a resinous substance which, according to Laurent, consisted of bitter almond oil, benzamide and benzoïn.

2. By aqueous or alcoholic potash, especially in presence of cyanide of potassium, or by pure cyanide of potassium, bitter almond oil is converted into benzoïn (*comp.* p. 24).

*Preparation.* The benzoïn which remains behind when crude bitter almond oil is rectified with potash or lime, is purified with hydrochloric acid and crystallised from alcohol.—2. One pt. of crude bitter almond oil is shaken up with a solution of 3 pts. hydrate of potash in 12 pts. of water, in a stoppered bottle, completely filled with the liquid. After three days, very small crystalline laminæ are deposited, but are redissolved by the oil on agitation; after fourteen days, the liquid is so loaded with it that it becomes thick; and after four weeks it becomes quite solid. The separated laminæ are removed from the liquid by filtration. (Robiquet & Boutron Charlard.)—3. When water is saturated with crude bitter-almond oil and a small quantity of potash added, the liquid after a few days deposits benzoïn in slender needles. (Wöhler & Liebig.) A solution of the oil in baryta or lime-water behaves in a similar manner. (Zinin.)—When bitter almond oil containing prussic acid is dissolved in a hot saturated solution of alcoholic potash, the mixture solidifies in a few minutes into a yellow crystalline mass of benzoïn merely contaminated with a little potash and a resinous matter, and easily purified by crystallisation from hot alcohol. The quantity of benzoïn thus obtained is nearly equal to that of the bitter almond oil used. If the proportion of hydrocyanic acid is too great, the mixture remains fluid for a long time, turns brown, and solidifies in a curdy mass, benzimide being then produced. If a sample treated with alcoholic

potash yields too little benzoïn, it is better to prepare pure bitter almond oil, and treat it as follows. (Zinin.) — 5. Pure bitter almond oil in contact with a weak alcoholic solution of cyanide of potassium or with alcoholic potash containing a few drops of prussic acid, is soon converted into benzoïn. (Zinin.)

*Properties.* Transparent, highly lustrous, regular six-sided prisms, sometimes with three rhombohedral faces. Melts at 120°, forming a colourless liquid which solidifies in a broadly laminated, radiating mass. Boils when strongly heated and volatilises undecomposed. Tasteless and inodorous.

| | | | Wöhler & Liebig. | Laurent. |
|---|---|---|---|---|
| 28 C | 168 | 79·24 | 79·08 | 78·65 |
| 12 H | 12 | 5·65 | 5·69 | 5·77 |
| 4 O | 32 | 15·11 | 15·23 | 15·58 |
| $C^{28}H^{12}O^{4}$ | 212 | 100·00 | 100·00 | 100·00 |

Isomeric with benzoate of benzyl and polymeric with bitter almond oil.—May be regarded as the aldide of benzilic acid (Laurent, *Méthode de Chimie*, 108).

*Decompositions.* 1. The vapour passed through a red-hot tube is converted into bitter almond oil. (Gerhardt, *Traité*, 3, 277.) [? J. L.]. — Burns in the air with a clear luminous flame. — 3. Heated in chlorine gas, it yields benzile and hydrochloric acid. (Laurent.)

$$C^{28}H^{12}O^{4} + 2Cl = C^{28}H^{10}O^{4} + 2HCl.$$

4. In contact with *bromine*, it becomes heated to the boiling point and gives off a large quantity of hydrobromic acid; and after the excess of bromine has been expelled by heat, there remains a brown viscid liquid which smells like bromide of benzoyl, but does not solidify like that compound. On dissolving it in alkali and adding hydrochloric acid, flakes separate consisting of delicate needles, which are neither benzoïn nor benzoic acid. (Wöhler & Liebig.) [Probably benzile. L.] 5. Heated with strong *nitric acid*, it yields benzile, with evolution of nitric acid. (Zinin.)

$$C^{28}H^{12}O^{4} + NO^{5} = C^{28}H^{10}O^{4} + 2HO + NO^{3}.$$

6. It is violently attacked by pentachloride of phosphorus, with formation of chlorophosphoric acid, and of various products difficult to obtain in the pure state. (Cahours, *N. Ann. Chim. Phys.* 23, 351.) — 7. With oil of vitriol, it forms a violet-blue solution, which soon turns brown, and when heated, first becomes green, then black and gives off sulphurous acid. (Wöhler & Leibig.) — 8. Benzoïn is not altered by boiling *potash-ley*. (Wöhler & Liebig.) Boiled with alcoholic potash, it yields benzilic acid [together with a volatile body having the odour of naphthalin. J. L.], (with evolution of hydrogen, according to Gerhardt, *Traité* 3, 277). Fused with hydrate of potash, it forms benzoic acid and gives off hydrogen. (Wöhler & Liebig.) — 9. In contact with aqueous *ammonia* for two months, it forms benzoïnamide; with alcoholic ammonia, it yields benzoïnam, benzoïnamide, and various products difficult to obtain in the pure state. Laurent passed ammoniacal gas into absolute alcohol in which benzoïn was immersed; after 4 or 5 months, the mixture contained: 1. Benzoïnam; 2. A body crystallising in rhombic tables

and soluble in 800—1000 pts. of alcohol; 3. Microscopic needles which appeared to be benzoïnamide; 4. Crystalline grains, which dissolved with tolerable facility in alcohol; 5. A soft resin which dissolved easily in alcohol, very easily in ether; 5 and part of 4 remain dissolved in the liquid. — Hydrosulphate of ammonia does not appear to act upon benzoïn. (Laurent.)

*Combinations.* Benzoïn is insoluble in cold water, but dissolves sparingly in boiling alcohol, and crystallises in slender needles on cooling. (Wöhler & Liebig.)

It dissolves in hot alcohol more readily than in cold alcohol. (Wöhler & Liebig.)

## ¶. Acetyl-benzoïn.

$$C^{32}H^{14}O^6 = C^4H^2O^2,C^{28}H^{12}O^4 = C^{28}H^{11}(C^4H^3O^2)O^4.$$

ZININ. *Ann. Pharm.* 104, 120.

*Formation and Preparation.* By the action of chloride of acetyl on benzoïn. — When chloride of acetyl is poured upon benzoïn (3 pts. of the former to 4 pts. of the latter) the action begins but slowly at ordinary temperatures; but on heating the mixture to 40° or 50°, the benzoïn dissolves, with evolution of hydrochloric acid. The heat must not be raised above 50° till the solution is complete, as otherwise the mass turns black and becomes difficult to purify. If the solution be then heated over the water-bath till nothing more is evolved at 100°; the product (whose weight amounts to about ⅘ of that of the benzoïn used) slowly solidifies on cooling to a crystalline mass which dissolves readily in alcohol and ether, and may be recrystallised therefrom.

*Properties.* Crystallises from the ethereal solution by slow evaporation in large rhombic prisms and six-sided tables; from the hot alcoholic solution in thin shining crystals. Melts below 100°, forming a colourless liquid which thickens on cooling, and remains viscid for a long time, but afterwards solidifies in a gummy mass, and slowly changes, especially in thin layers, into a white crystalline mass.

| | | | Zinin. |
|---|---|---|---|
| 32 C | 192 | 75·59 | 75·60 |
| 14 H | 14 | 5·51 | 5·58 |
| 6 O | 48 | 18·90 | 18·82 |
| $C^{32}H^{14}O^6$ | 254 | 100·00 | 100·00 |

The substance analysed was recrystallised from alcohol and ether.

The compound is not acted upon by sulphuric or hydrochloric acid. Strong nitric acid produces with it a mixture of two nitro-products in the form of a viscid, transparent, nearly colourless mass, insoluble in water, but dissolving easily in alcohol and still more in ether; the ethereal solution deposits a nitro-compound in crystalline crusts. — Acetyl-benzoïn is not acted upon by aqueous potash, but with alcoholic potash it yields a mixture of acetate and benzoate of potash.

Insoluble in water, but dissolves readily in *alcohol* and *ether*, warm alcohol dissolving nearly twice its weight of the compound.

## ¶. Benzoyl-benzoïn.

$$C^{42}H^{16}O^{6} = C^{14}H^{6}O^{2},C^{28}H^{12}O^{4} = C^{28}H^{11}(C^{14}H^{5}O^{2})O^{4}.$$

ZININ. *Ann. Pharm.* 102, 116.

*Formation and Preparation.* By the action of chloride of benzoyl on benzoïn. No action takes place at ordinary temperatures, but if the mixture be heated till the benzoïn is completely dissolved and no more hydrochloric acid is evolved, even at a temperature near the boiling point of chloride of benzoyl, a slightly yellowish oily liquid is obtained, which on cooling deposits benzoyl-benzoïn in warty, laminar, crystalline masses, and if the proportion of chloride of benzoyl is not too great, the entire liquid sometimes solidifies into a white mass. To purify this product, it is poured while yet liquid into cold alcohol of 75 per cent. (in which it dissolves but sparingly) and diffused through it by brisk agitation; it is thereby obtained in the form of a crystalline powder, which is separated from the liquid when quite cold and washed on a filter with cold alcohol. — The quantity of benzoyl-benzoïn obtained is always the same, viz. 1 At., whether 1, 2 or 3 At. chloride of benzoyl be used to 1 At. benzoïn; but if only 1 At. chloride of benzoyl be used, it is necessary to heat the mixture more strongly and for a longer time, and it is then apt to turn dark yellow or even brown.

*Properties.* Crystallises on cooling from boiling alcohol in thin colourless needles resembling benzoïn, and from ether by spontaneous evaporation in large shining rhombic prisms. Melts at 125°, forming a colourless liquid which on cooling becomes viscid and tenacious and then solidifies in an amorphous mass, which becomes opaque and crystallises slowly when left to itself, more quickly when rubbed with a hard body, and still more when warm alcohol or ether is poured upon it.

| | | | | Zinin. |
|---|---|---|---|---|
| 42 C | 252 | 79·74 | | 79·79 |
| 16 H | 16 | 5·06 | | 5·18 |
| 6 O | 48 | 15·20 | | 15·03 |
| $C^{42}H^{16}O^{6}$ | 306 | 100·00 | | 100·00 |

*Decompositions.* The compound is not acted upon by hydrochloric or by dilute sulphuric acid, but strong sulphuric acid decomposes it with the aid of heat. Chlorine has no action upon it even in the melted state. — With nitric acid it forms nitrobenzoyl-benzoïn, $C^{42}H^{15}XO^{6}$. Aqueous potash does not act upon benzoyl-benzoïn, but alcoholic potash dissolves it with violet colour, and when the action assisted by boiling is complete, a mixture of benzoate and benzilate of potash is obtained.

*Combinations.* Insoluble in water, very sparingly soluble in cold *alcohol*, but dissolves in six times its weight of boiling 80 per cent. alcohol. Dissolves readily and abundantly in *ether*, especially when heated.

Dissolves without decomposition in chloride of benzoyl.

## ¶. Nitrobenzoyl-benzoïn.

$C^{42}NH^{15}O^{10} = C^{42}XH^{15}O^{6}$.

ZININ. *Ann. Pharm.* 102, 118.

*Formation and Preparation.* By the action of fuming nitric acid on benzoyl-benzoïn. — When benzoyl-benzoïn is added to nitric acid (either colourless or yellow) of sp. 1·51, heat is evolved and the substance melts; if only a small quantity of nitric acid is present, the benzoyl-benzoïn dissolves in it on the application of heat, and separates out again in its original state on cooling; but if 1½ pts. or more of nitric acid be added to 1 pt. of benzoyl-benzoïn, the latter dissolves without external heating, and with scarcely any evolution of red vapours; and on pouring the yellowish solution into cold water, a resinous body is deposited which is hard while cold, but melts easily in hot water. This substance is washed with water as long as the water thereby acquires a yellowish colour and acid reaction, and the washed product (amounting to ⅔ of the benzoyl-benzoïn used) is treated with cold ether, which dissolves a portion and leaves nitrobenzoyl-benzoïn in the form of a crystalline powder amounting to rather more than half the weight of the benzoyl-benzoïn; it is purified by recrystallisation from boiling alcohol. — The ethereal solution leaves on evaporation a thick oil, sparingly soluble in alcohol, which appears also to be a nitro-compound.

*Properties.* Crystallises from boiling alcohol in white shining scales composed of rhombic plates aggregated in scalariform groups. Melts at 137°, forming a colourless liquid, which solidifies at 110°, in a granular mass like starch-sugar; in thin layers it solidifies to a gummy mass, which however quickly becomes opaque and crystalline when rubbed with a hard body.

| | | | Zinin. |
|---|---|---|---|
| 42 C | 252 | 69·80 | 69·77 |
| N | 14 | 3·88 | 4·00 |
| 15 H | 15 | 4·15 | 4·22 |
| 10 O | 80 | 22·17 | 22·01 |
| $C^{42}NH^{15}O^{10}$ | 361 | 100·00 | 100·00 |

The compound is insoluble in water. Strong nitric acid dissolves it readily and in large quantity, especially at a gentle heat, and without decomposition; but on boiling the liquid, a new body is formed, which dissolves pretty readily in ether, but is less soluble in alcohol than the nitrobenzoylbenzoïn, and separates in the pulverulent form as the solution cools.

Nitrobenzoylbenzoïn dissolves in 12 pts. of boiling *alcohol*, and separates out almost completely on cooling: it is insoluble in ether. ¶.

## Stilbous Acid. $C^{30}H^{12}O^{6}$. ?

ROBIQUET & BOUTRON CHARLARD. (1830.) *Ann. Chim. Phys.* 44, 371.
LIEBIG & WINCKLER. *Ann. Pharm.* 18, 324; *Pogg.* 41, 389.
LIEBIG & PELOUZE. *Ann. Pharm.* 19, 289; *Ann. Chim. Phys.* 63, 145.
LAURENT. *Ann. Chim. Phys.* 65, 193; *J. pr. Chem.* 12, 416.—*N. Ann. Chim. Phys.* 1, 309; *Ann. Pharm.* 38, 335.—*Rev. scientif.* 10, 120; *J. pr. Chem.* 27, 310.—*Rev. scient.* 16, 373; *J. pr. Chem.* 35, 429.—*Compt. rend.* 22, 789.
LAURENT & GERHARDT. *Compt. chim.* 1850, 117.

***Stilbinige Säure, benzoesaures Bittermandelöl, benzoesaurer Benzoylwasserstoff, Benzoate d'hydrure de benzoïle, Acide stilbeux, Suroxide de stilbène.***—Appears to have been first observed by Stange (*Repert.* 14, 369) in bitter almond oil which had been treated with chlorine gas, but was first recognised as a peculiar substance distinct from benzoïn by Liebig & Winckler.

*Formation.* By treating bitter almond oil, cherry-kernel oil, or laurel oil, containing prussic acid with moist chlorine gas (Robiquet & Boutron Charlard, Liebig & Winckler, Laurent), — or with fuming oil of vitriol (Laurent), — or with chloride of sulphur. (Laurent.)

*Preparation.* 1. Moist chlorine gas is absorbed by bitter almond oil (or laurel oil), with considerable rise of temperature, and the clear greenish yellow liquid saturated with chlorine deposits, after a few hours, small crystals which often cause the entire liquid to assume the form of a compact solid mass. On treating this mass with ether, a white crystalline powder remains undissolved. (Robiquet & B. Charlard, Liebig & Winckler.) — 2. When three measures of commercial bitter almond oil are mixed with one measure of fuming oil of vitriol, great heat is evolved; and the brown liquid thickens and solidifies in the cold to a crystalline mass, which, on being shaken with water, separates into two layers; the lower consisting of sulphuric acid with a small quantity of bitter almond oil, while the upper is semi-solid and yields, when treated with a small quantity of ether-alcohol—which takes up any bitter almond oil that may have remained unaltered—a white crystalline powder, which, when recrystallised from hot alcohol, forms either rectangular prisms or slender needles. (Laurent.) — 3. Bitter almond which did not yield any product when subjected to the process just described, was, after being treated with oil of vitriol, immediately mixed with ether, and gradually neutralised with ammonia; an oily layer then separated, which solidified after a while, and yielded rectangular prisms when boiled with alcohol. (Laurent.) — 4. Bitter almond oil becomes strongly heated in contact with chloride of sulphur, and evolves hydrochloric acid; and if the oily product containing a few needles, be treated after a few hours with a mixture of ether and alcoholic ammonia, three layers are formed, the lower of which is a thick mass chiefly consisting of sulphur, the middle an alcoholic solution of sal-ammoniac, and the upper an ethereal solution of unaltered bitter almond oil and stilbous acid. (Laurent.)

*Preparation.* Crystallises in two different forms: the products 1, 3 and 4, and sometimes also 2, crystallise in dazzling white, transparent

rectangular prisms, whose terminal faces are replaced by two faces intersecting one another at an obtuse angle and resting on the horizontal edges of the prisms; one of these faces generally predominates and gives the crystals the aspect of an oblique rectangular prism. (Liebig & Winckler, Laurent.) The crystals obtained by (2) are small rhomboïdal prisms whose terminal faces are replaced by two faces intersecting at an acute angle and resting on the edges of the prism. (Laurent.) The two forms cannot be made to pass one into the other by recrystallisation from hot alcohol; but if the rectangular crystals be kept for a few seconds in the melted state and then dissolved in hot alcohol, the solution on cooling deposits the rhomboïdal prisms. (Laurent.) The salt melts when heated at about 160° (Robiquet & B. Charlard) without volatilising, and solidifies on cooling in an opaque radiated mass or a transparent gum. (Laurent.) Tasteless and nearly inodorous; without action on vegetable colours.

*Formulæ and Calculations according to:*

| I. | | Liebig. | II. | | Laurent. |
|---|---|---|---|---|---|
| 42 C | 252 | 75·45 | 56 C | 336 | 70·36 |
| 18 H | 18 | 5·39 | 24 H | 24 | 5·46 |
| 8 O | 64 | 19·16 | 10 O | 80 | 18·18 |
| $C^{42}H^{18}O^{8}$ | 334 | 100·00 | $C^{56}H^{24}O^{10}$ | 440 | 100·00 |

| III. | | Laurent & Gerhardt. | IV. | | |
|---|---|---|---|---|---|
| 44 C | 264 | 76·30 | 30 C | 180 | 75·0 |
| 18 H | 18 | 5·20 | 12 H | 12 | 5·0 |
| 8 O | 64 | 18·50 | 6 O | 48 | 20·0 |
| $C^{44}H^{18}O^{8}$ | 346 | 100·00 | $C^{30}H^{12}O^{6}$ | 240 | 100·0 |

*Analyses according to:*

| | Liebig. | | | Liebig & Pelouze. |
|---|---|---|---|---|
| | *a.* | *b.* | *c.* | *d.* |
| C | 74·59 | 74·86 | 74·92 | 75·27 |
| H | 5·42 | 5·66 | 5·69 | 5·64 |

| | Laurent. | | | | | |
|---|---|---|---|---|---|---|
| | *e.* | *f.* | *g.* | *h.* | *i.* | *k.* |
| C | 74·2 | 74·4 | 74·6 | 75·0 | 75·82 | 76·20 |
| H | 5·6 | 5·4 | 5·3 | 5·4 | 5·47 | 5·45 |

For the analyses *a*, *b*, *c*, *d* and *k*, the substance was prepared by (1); for *e*, *f*, *g*, *h* and *i*, by (2); the analysis *i*, was made by Laurent eight years later than the rest.—Calculation I, is founded on analyses *a* . . . *h*, and regards the substance as benzoate of hydride of benzoyl, $2C^{14}H^{5}O^{2},C^{14}H^{6}O^{4}$: II, is founded on the analyses *i*, *k*, and assumes the formula, $3C^{14}H^{6}O^{2},C^{14}H^{6}O^{4}$. Laurent & Gerhardt observe (*Compt. chim.* 1850, 117), that these views do not explain the formation of the compound by the action of oil of vitriol, and they suggest that its formation takes place with the agency of hydrocyanic acid (like the formation of mandelic acid) as represented by the following equation (Calculation III):

$$3C^{14}H^{6}O^{2} + C^{2}NH + 2HO = C^{44}H^{18}O^{8} + NH^{3};$$

at the same time they direct attention to the decomposition (4). Calculation IV, agrees better with the greater number of the analyses. According to this view, the action of the oil of vitriol, or of the hydrochloric acid resulting from the moist chlorine converts the hydrocyanic acid into formic acid, which unites with 2 At. bitter almond oil or 1 At. benzoin, while 2 At. water are separated (compare *Decomposition* 4, and the potash-compound):

$$C^{30}H^{12}O^{6} = C^{14}HO^{2} = C^{2}H^{2}O^{4} - 2HO.$$

The formation of benzoic acid on heating the compound with alcoholic potash does not necessitate the assumption that the compound actually contains benzoic acid, inasmuch as that acid is produced, under the same circumstances, from bitter almond oil. (p. 23).

*Decompositions.* 1. Stilbous acid yields by distillation first a yellowish, then a greenish oil, which dissolves in ether, leaving elongated laminæ. (Laurent) — 2. *Chlorine gas* passed through fused stilbous acid forms hydrochloric acid and an oil which solidifies partially after a while, and is partly dissolved when boiled with water; the solution on cooling yields small right rectangular prisms, which crystallise in the same form after fusion, burn with a flame which has no green edges — therefore do not contain chlorine — may be volatilised without decomposition (therefore are not mandelic acid, L.), and form with nitric acid, a solution, yielding by evaporation a substance which dissolves in alcohol and ether as well as in ammonia, but does not appear to be a definite compound. The portion of the oil insoluble in boiling water dissolves in alcohol and in ether, and for the most part also in boiling potash. The still hot potash-solution forms when saturated with acids, a laminated crystalline precipitate, which melts when heated, solidifies in a fibrous mass on cooling, dissolves in alcohol and ether, but does not consist of benzoic acid [stilbesic acid? L.] (Laurent). — 3. Stilbous acid is slowly decomposed by boiling *nitric acid;* the solution does not contain benzoic acid. (Laurent.) — 4. Heated with *oil of vitriol,* it gives off carbonic oxide; and the residue treated with water yields a thick brown mass, which smells like bitter almonds, and dissolves partially in ammonia. — 5. Boiled with alcoholic *potash,* it yields benzoate of potash. (Liebig.) — 6. In contact with alcoholic ammonia it remains unaltered. (Laurent.)

*Combinations. Stilbite of Potash.* — Formed by the action of very strong potash-ley on stilbous acid, as an oily-liquid, which, when exposed to the air, gives off 8 or 10 per cent. of water, and solidifies in a fibrous mass, which at a temperature somewhat above 100°, gives off 25 p. c. (about 10 At.) water and leaves a solid tumefied mass containing 17·1 p. c. potash.

| | | | Laurent. |
|---|---|---|---|
| $C^{30}H^{11}O^{5}$ | 231·0 | 83·04 | |
| KO | 47·2 | 16·96 | 17·2 |
| $C^{30}H^{11}KO^{6}$ | 278·2 | 100·00 | |

If the compound were $C^{42}H^{17}KO^{8}$ (according to I), it should contain 12·68 per cent. of potash, whereas the formula $C^{36}H^{22}K^{2}O^{10}$ (according to II), or, according to Laurent, $C^{28}H^{11}KO^{5}$, requires 18·28 p. c. KO, and the formula $C^{44}K^{17}KO^{8}$ (according to III), requires 12 p. c. KO.

Stilbous acid is insoluble in cold alcohol, but dissolves abundantly in hot *alcohol,* and readily in *ether.*

## Stilbesic Acid.

LAURENT. *Rev. scient.* 16, 387; *J. pr. Chem.* 35, 430.
LAURENT & GERHARDT. *Compt. chim.* 1850, 117.

*Acide stilbeseux, Suroxide de stilbèse.*

When bitter almond oil is treated with chlorine gas, aided by heat towards the end of the process, the whole solidifies on cooling into a crystalline mixture of benzoic acid, stilbesic acid, a body crystallising in slender needles, and chloride of benzoyl; and if the chloride of benzoyl be allowed to drain on a funnel stopped with coarsely pounded glass, the mass pressed between paper and treated with cold ether-alcohol, stilbesic acid remains behind, and may be crystallised by solution in boiling ether and spontaneous evaporation.

Oblique rhombic prisms. *Fig.* 84, without *f* and *i*; *fig.* 84 without *f* and *m*; $i : m = 126° 30'$; $m : u = 138°$; $u : u = 96°$; $a : m = 96$. Melts at 145°, and if the whole has not been fused, solidifies at the same temperature, but after complete fusion, not till cooled down to the ordinary temperature, forming a transparent gum which when carefully heated, slowly crystallises in opaque radiated nodules.

| | | | Laurent. |
|---|---|---|---|
| 28 C | 168 | 71·80 | 71·58 |
| 10 H | 10 | 4·28 | 4·33 |
| 7 O | 56 | 23·92 | 24·09 |
| $C^{28}H^{10}O^{7}$ | 234 | 100·00 | 100·00 |

Laurent supposes that, in the formation of stilbesic acid, 2 At. bitter almond oil have taken up 1 At. oxygen to form stilbous acid, and that in this compound 2 At. H are replaced by O, water being at the same time decomposed: for although the chlorine used was dry, the hydrochloric acid vapours above the oil had nevertheless condensed moisture from the air. This view takes no account of the decomposition by oil of vitriol. According to Laurent & Gerhardt, the prussic acid contained in the bitter almond oil exerts an influence on the formation of stilbesic as well as of stilbous acid. Any more definite conclusion appears for the present unattainable.

Stilbesic acid yields by distillation an oil which on cooling deposits crystals, apparently a product of decomposition. (Laurent.) — Heated with oil of vitriol, it gives off carbonic oxide gas; water added to the residue separates benzoic acid. (Laurent & Gerhardt.) — It dissolves in *potash* and in *ammonia* and is precipitated therefrom by water. (Laurent.)

*Stilbesate of Silver.* — The boiling ammoniacal solution mixed with nitrate of silver forms shining scales. (Laurent.)

| | | | Laurent. |
|---|---|---|---|
| $C^{28}H^{8}O^{7}$ | 232 | 51·79 | |
| 2 Ag | 216 | 48·21 | 48·7 |
| $C^{28}H^{8}Ag^{2}O^{7}$ | 448 | 100·00 | |

The acid dissolves very sparingly in alcohol and in ether. The solution does not redden litmus. (Laurent.)

The solution in ether-alcohol obtained in the preparation of stilbesic acid yields by evaporation, benzoic acid and slender needles. These when freed from benzoic acid by dilute ammonia and purified by recrystallisation from cold ether, form long, shining, needle-shaped crystals united in tufts; after fusion, they solidify in an amorphous mass, which when gently heated crystallises in microscopic spherical nodules. These crystals dissolve in boiling ammonia and are precipitated therefrom by acids. (Laurent.) When distilled, they yield another substance which crystallises in distorted needles.

## Benzilic Acid.

$C^{28}H^{12}O^{6} = C^{28}H^{12}O^{2},O^{4}$.

LIEBIG. (1838.) *Ann. Pharm.* 25, 25.
ZININ. *Ann. Pharm.* 31, 329.

*Acide stilbique, Stilbinsäure.*

*Formation and Preparation.* Hot alcoholic potash is added to benzoïn or [better, J. L.] to benzoyl, till a fresh addition no longer causes any blue colouring; the alcohol is then driven off, and the alkaline liquid diluted with water, mixed at the boiling heat with excess of hydrochloric acid, and filtered from any oil or resin that may be separated. The filtrate becomes milky on cooling and deposits crystals of the acid. (Liebig.) Benzile or benzoïn is dissolved in boiling and tolerably concentrated alcoholic potash, in such quantity as to leave the liquid distinctly alkaline. The mixture is then boiled till a portion of it mixes with water without turbidity; the liquid evaporated to dryness over the water-bath; the residue exposed to air rich in carbonic acid till the potash is completely saturated with that acid [the conversion of the caustic potash into carbonate may however be better effected by adding carbonate of ammonia before evaporating; J. L], the mass treated with alcohol; the solution separated from the carbonate of potash, mixed with water; the alcohol distilled off, the remaining liquid boiled with animal charcoal till it becomes colourless or retains only a slight yellowish tint, and then filtered; the charcoal washed with hot water; and the solution left to evaporate to the crystallising point. The crystallised potash-salt is dissolved in water; the solution poured into an excess of boiling and largely diluted hydrochloric acid; and the mixture boiled till the turbidity produced on mixing has completely disappeared. If the liquid be then left to cool slowly, it becomes opalescent and filled with long needles of benzoic acid. (Zinin.)

*Properties.* Hard, shining, transparent needles. Inodorous. Has a sourish, bitter, metallic taste. Melts at 120°, forming a colourless liquid. (Zinin.) Has a strong acid reaction.

| | | | Liebig. | Zinin. |
|---|---|---|---|---|
| 28 C | 168 | 73·68 | 73·09 | 73·14 |
| 12 H | 12 | 5·26 | 5·35 | 5·31 |
| 6 O | 48 | 21·06 | 21·56 | 21·55 |
| $C^{28}H^{12}O^{6}$ | 228 | 100·00 | 100·00 | 100·00 |

*Decompositions.* 1. Heated above the melting point, it turns red, and emits a peculiar odour and a violet-red vapour, which condenses into a brown-red oil having a burning sharp taste, distilling without alteration, insoluble in water, but dissolving easily and with red colour in alcohol and ether; the solution is rendered turbid by water, but not decolorised, it is decolorised by potash ammonia and nitric acid, but not by hydrochloric or sulphuric acid. (Zinin.) — 2. To oil of vitriol, benzilic acid and its salts impart a fine carmine colour, which is not easily destroyed by heat; it disappears on addition of water, but reappears on evaporation. (Liebig, Zinin.) — 3. With pentachloride of phosphorus, it yields phosphoric acid, chlorophosphoric acid, and chlorobenzile. (Cahours.) — 4. Benzilate of potash when strongly heated, gives off white vapours which condense to a colourless oil, smelling like naphthalin, having a rough burning taste, distilling without alteration, easily soluble in alcohol, and precipitated therefrom by water. The residue contains charcoal and carbonate of potash. (Zinin.)

*Combinations.* The acid dissolves sparingly in cold, more readily in boiling water.

It dissolves in hot nitric acid, and is precipitated unaltered by water. (Zinin.)

*Benzilate of Potash.* — (*Preparation, vid. sup.*) Colourless transparent crystals, easily soluble in water and alcohol, insoluble in ether. The aqueous solution, evaporated at a strong heat, solidifies in a mass consisting of narrow tables. Melts above 200°, forming a colourless liquid, which solidifies on cooling. It is decomposed at a high temperature (*vid. sup.*). — Anhydrous. Contains 17·59 per cent. of potash, and is therefore $C^{28}H^{11}KO^{6}$. (Zinin.)

*Benzilate of Lead.* — Obtained by dropping a solution of neutral acetate of lead into the aqueous acid as long as any precipitate is produced. White powder, unalterable at 100°; when heated, it melts into a red liquid and gives off violet-red vapours. Dissolves to a slight extent in hot water. Contains 32·87 per cent. of oxide of lead, and is therefore $C^{28}H^{11}PbO^{6}$. (Zinin.)

*Benzilate of Silver.* — Obtained by precipitating nitrate of silver with the ammonia or potash salt. White crystalline powder. At 100°, it assumes a smalt-blue colour, without loss of weight, but after some time becomes brown-red and begins to decompose; at a higher temperature it melts, gives off violet-red vapours, and leaves metallic silver. Slightly soluble in hot water.

| | | | Liebig. | Zinin. |
|---|---|---|---|---|
| Ag | 108 | 32·24 | 32·25 | 31·98 |
| 28 C | 168 | 50·15 | | 49·53 |
| 11 H | 11 | 3·28 | | 3·37 |
| 6 O | 48 | 14·33 | | 15·12 |
| $C^{28}H^{7}AgO^{6}$ | 335 | 100·00 | | 100·00 |

The acid dissolves in *alcohol* and in *ether*

## Chlorobenzile.

$C^{28}ClH^{11}O^{4} = C^{28}ClH^{11},O^{4}$.

CAHOURS. (1849.) *N. Ann. Chim. Phys.* 23, 350; *J. pr. Chem.* 45, 146;—abstr. *Ann. Pharm.* 70, 46.

Pentachloride of phosphorus acts violently, with the aid of heat, upon benzilic acid, a large quantity of hydrochloric acid being evolved, and the product, when distilled, yielding chlorophosphoric acid at 111°, and from 250° upwards, chlorobenzile, which is washed with cold water, dried by chloride of calcium and rectified.

Colourless liquid, heavier than water, boiling at about 270°, and having a powerful odour.

| | | | | Cahours. |
|---|---|---|---|---|
| 28 C | 168·0 | 68·18 | | 68·39 |
| 11 H | 11·0 | 4·46 | | 4·48 |
| Cl | 35·4 | 14·35 | | 14·00 |
| 4 O | 32·0 | 13·01 | | 13·13 |
| $C^{28}H^{11}ClO^{4}$ | 246·4 | 100·00 | | 100·00 |

In contact with moist air, it is quickly converted into hydrochloric and benzilic acid. With hot strong potash-ley, it quickly yields chloride of potassium and benzilate of potash. With ammonia and aniline it forms crystalline products (benzilamide and benzilanilide?).

## Benzile. $C^{28}H^{10}O^{4}$.

LAURENT. (1835.) *Ann. Chim. Phys.* 59, 402; *Ann. Pharm.* 17, 91; *Pogg.* 36, 501; *J. pr. Chem.* 35, 46.
LIEBIG. *Ann. Pharm.* 25, 25.
ZININ. *Ann. Pharm.* 34, 188.—*J. pr. Chem.* 33, 35.
GREGORY. *Compt. chim.* 1845, 308.

*Benzoyl, Benzyl, Sousoxyde de Stilbèse.*

*Formation.* By the action of chlorine or nitric acid upon benzoïn.—Gregory, on one occasion, obtained benzile, in attempting to prepare benzoïn by heating bitter almond oil with hydrocyanic acid and alcoholic potash.

*Preparation.* 1. By passing chlorine gas over fused benzoïn, as long as hydrochloric acid is evolved, and crystallising the product from alcohol. (Laurent.) — 2. When 1 pt. of dry benzoïn is gently heated with 2 pts. of strong colourless nitric acid, nitrous acid is copiously evolved, and the benzoïn melts into a clear yellow oil which rises to the surface of the liquid and consists of pure benzile. (Zinin.)

*Properties.* Yellowish, nearly colourless. Crystallises from the alcoholic or ethereal solution by spontaneous evaporation in regular six-

sided prisms. (P. ∞P. oP or R. ∞R.) (*Fig.* 137, *fig.* 146.) $\sigma : \sigma = 120°$; $r^1$ and $r^3 : \sigma = 134°$; $r^2 : \sigma = 152$. The crystals commonly have in the middle a hollow space with six sides parallel to the faces of the prism. (Laurent.) Conchoïdal fracture. After fusion between 90° and 92°, it solidifies in a fibrous mass. Volatilises without decomposition. Inodorous and tasteless.

| | | | Laurent. | Liebig. |
|---|---|---|---|---|
| 28 C | 168 | 80·00 | 79·61 | 79·29 |
| 10 H | 10 | 4·76 | 4·84 | 4·73 |
| 4 O | 32 | 15·24 | 15·55 | 15·98 |
| $C^{28}H^{10}O^4$ | 210 | 100·00 | 100·00 | 100·00 |

*Decomposition.* 1. Burns with a red sooty flame. (Laurent.) — 2. It is not altered by boiling with nitric acid. (Laurent.) — 3. It is not decomposed by boiling with potash-ley (Laurent); but when boiled with alcoholic potash it turns blue and forms benzilic acid. (Liebig.) — 4. The vapour passed over red-hot lime yields an oil and a small quantity of charcoal. (Laurent.) — 5. When an alcoholic solution of benzile is mixed with aqueous *ammonia,* a white fine-grained precipitate of azobenzile ($C^{42}NH^{15}O^2$) is produced; at the same time benzoate of ethyl is formed, and a substance which dissolves readily in alcohol, and crystallises in small needles. The latter substance is formed in larger quantity when the alcoholic solution of benzile is gradually mixed with small quantities of aqueous ammonia, and kept boiling all the while, till the liquid becomes turbid. (Zinin.) When an alcoholic solution of benzile saturated at a high temperature, is saturated while yet warm with dry ammoniacal gas, and suffered to cool during the passage of the gas, a white sediment is produced, which, in the course of 24 hours, becomes covered with small needles, while other products remain in solution. The products thus formed are imabenzil, benzilimide, benzilam and an oil very soluble in alcohol. (Laurent.) — 6. *Sulphuretted hydrogen* forms, with abundant deposition of sulphur, a yellow oil smelling of garlic; this oil, however, is more readily formed by distilling benzoyl with hydrosulphate of ammonia. (Zinin.). By the action of hydrosulphate of ammonia on benzile, two or three different substances are formed, among which hydrobenzile (p. 185) occurs. (Zinin.) — 7. Benzile fused with *potassium* gives off violet vapours and leaves a carbonaceous residue.

*Combinations.* Insoluble in water. Dissolves in hot oil of vitriol and is precipitated therefrom by water. (Laurent.)

*Hydrocyanate of Benzile.* — When to a solution of benzile in boiling alcohol, there is added a quantity of nearly anhydrous prussic acid about equal to that of the benzile, the mixture, on being left to itself, deposits white shining rhombic tables produced from a combination of the rhombohedron with a right prism. (Zinin.)

| | | | Zinin. |
|---|---|---|---|
| 32 C | 202 | 73·72 | 72·96 |
| 12 H | 12 | 4·38 | 4·58 |
| 2 N | 28 | 10·22 | 10·39 |
| 4 O | 32 | 11·68 | 12·07 |
| $C^{28}H^{10}O^4,2C^2NH$ | 274 | 100·00 | 100·00 |

Melts and decomposes when heated, leaving a residue of benzile. Heated with nitric acid or ammonia, it yields benzile. The alcoholic solution mixed with nitrate of silver forms cyanide of silver, and benzile crystallises from the solution. The alcoholic solution heated with mercuric oxide reduces it, and at the same time, the presence of benzoate of ethyl becomes perceptible. The compound is not altered by boiling with water or with salts.

Benzile dissolves readily in *alcohol* and in *ether*.

*Appendix to Benzile.*

## Hydrobenzile. $C^{28}H^{12}O^{2}$.

ZININ. (1844.) *J. pr. Chem.* 33, 35.

When benzile is treated with hydrosulphate of ammonia, two or three different bodies are produced, one of which forms crystals in the shape of concavo-convex lenses united in spiral geodes. Melts at 47° forming a colourless liquid which may be distilled without alteration, and solidifies in the crystalline form at 42°. Smells like bitter almond oil and has a sweetish burning taste.

| | | | | | Zinin. |
|---|---|---|---|---|---|
| 28 C | 168 | | 85·71 | | 85·75 |
| 12 H | 12 | | 6·12 | | 6·27 |
| 2 O | 16 | | 8·17 | | 7·98 |
| $C^{28}H^{12}O^{2}$ | 196 | | 100·00 | | 100·00 |

Boiled with nitric acid, it forms a yellow resin, which is not completely precipitated by water.

It is not altered by boiling with solution of potash. It does not give off ammonia when fused with hydrate of potash. It dissolves in alcoholic potash, and appears not to be altered by boiling.

It is but slightly attacked by chlorine gas.

Dissolves readily in oil of vitriol, and is precipitated by water in its original state.

Insoluble in water, but dissolves readily in *alcohol* and *ether*.

## Picril.

$C^{42}NH^{14}O^{4}$ or $C^{42}NH^{15}O^{4}$ (= $C^{42}NH^{15}O^{2},O^{2}$). ?

LAURENT. (1844.) *Rev. scient.* 18, 201; *J. pr. Chem.* 35, 448.—*N. Ann. Chim. Phys.* 19, 369; *J. pr. Chem.* 40, 407; *Ann. Pharm.* 62, 108.

*Preparation.* The ethereal liquid from which crude stilbene (p. 167) has separated on cooling, yields by spontaneous evaporation a very dark-coloured oil and brown crystalline grains which, after the addition of a small quantity of ether, must be separated quickly from the liquid. The solution still yields by evaporation a few more crystalline granules, which

may be washed with a mixture of ether and alcohol; the mother-liquor is again left to evaporate as long as any crystalline granules separate. The crystalline granules, when dissolved in ether and several times recrystallised, yield very beautiful colourless crystals.

Colourless octohedrons belonging to the oblique prismatic system, and having their summits and the smaller edges of their bases truncated. (+P : − P on the lateral edges = 112°; − P ; + P on the edges of the base = 117°; + P : ∞P = 139° 30′ : oP : + P = 133° 30′; oP : P = 121° 30′.

Melts at a gentle heat and solidifies into an opaque gummy mass on cooling.

| Calculation I. | | | Calculation II. | | |
|---|---|---|---|---|---|
| 42 C | 252 | 80·80 | 42 C | 252 | 80·52 |
| N | 14 | 4·50 | N | 14 | 4·47 |
| 14 H | 14 | 4·50 | 15 H | 15 | 4·78 |
| 4 O | 32 | 10·20 | 4 O | 32 | 10·23 |
| $C^{42}NH^{14}O^4$ | 312 | 100·00 | $C^{42}NH^{15}O^4$ | 313 | 100·00 |

Analyses.

| | a. | b. | c. |
|---|---|---|---|
| C | 80·80 | 80·45 | 80·27 |
| N | 4·76 | | |
| H | 4·59 | 4·70 | 4·77 |
| O | 9·85 | | |
| | 100·00 | | |

From analysis *a*, Laurent formerly deduced the formula I, according to which, picril might be a compound of benzolone and cyanogen ($C^{42}NH^{14}O^4 = C^{40}H^{14}O^4 + C^2N$); analysis *b* was afterwards made with somewhat yellowish crystals; *c* with perfectly colourless crystals.

*Decompositions.* Pulverised picril immediately forms with *bromine* a gummy mass, a small quantity of hydrobromic acid escaping at the same time. The product, after being purified from free bromine by washing with water, then dissolved in ether, reprecipitated by alcohol, and freed from adhering ether and alcohol by gentle heating in vacuo, forms a colourless, transparent, brittle resin, which contains 61·36 p. c. C, 3·33 p. c. H, and 24·30 p. c. Br. and according to Laurent, is a mixture of $C^{42}NBrH^{14}O^4$ and $C^{42}NBr^2H^{13}O^4$. It appears to be capable of distilling partly without alteration, but at last a small quantity of hydrobromic acid is evolved, and charcoal also in small quantity left behind. — *Chlorine*, aided by heat, acts like bromine, evolving hydrochloric acid, and forming a soft resinous mass which dissolves readily in ether and is precipitated therefrom by alcohol; it contains 68·2 p. c. C and 3·8 p. c. H, and is therefore a mixture of $C^{42}NClH^{14}O^4$ and $C^{42}NCl^2H^{13}O^4$.

3. Picril boiled with *nitric acid* is at first converted into a yellow resinous mass, which, after boiling for some time, dissolves and is converted into nitropicril. — 4. When picril is boiled with aqueous *chromic acid*, a brown mixture is produced, partially soluble in ether. The insoluble portion may be sublimed in white laminæ at a high temperature.

5. Picril is decomposed by *potassium* with the aid of heat, and ether extracts from the product a body which crystallises in rhombs. — 6. It is not decomposed by boiling with alcoholic potash.

Picril dissolves very readily in *ether*, much less readily in *alcohol*.

## Nitropicril.

$C^{42}NX^{3}H^{11}O^{4}$ or $C^{42}NX^{3}H^{12}O^{4}$.

LAURENT. *loc. cit.*

When picril is boiled with nitric acid till the whole is dissolved, the solution on cooling deposits a yellow somewhat crystalline powder, a little more of which separates on addition of water.

| | | |
|---|---|---|
| 42 C | 252 | 56·30 |
| 4 N | 56 | 12·50 |
| 11 H | 11 | 2·45 |
| 16 O | 128 | 28·75 |
| $C^{12}N^{4}H^{11}O^{16}$ | 447 | 100·00 |

| | | | Laurent. |
|---|---|---|---|
| 42 C | 252 | 56·25 | 56·80 |
| 4 N | 56 | 12·50 | 12·60 |
| 12 H | 12 | 2·68 | 2·37 |
| 16 O | 128 | 28·57 | 28·23 |
| $C^{42}N^{4}H^{12}O^{16}$ | 448 | 100·00 | 100·00 |

When heated it decomposes with emission of light.

It dissolves very sparingly in *alcohol*, very readily in *ether*.

## Thionessal.

$C^{26}H^{9}S = C^{12}H^{3}S,C^{14}H^{6}$.

LAURENT. (1844.) *Rev. scient.* 18, 197; *J. pr. Chem.* 35, 44.

*Sulfessal.*

*Formation and Preparation.* In the dry distillation of sulphide of stilbene or of the crude product of the action of hydrosulphate of ammonia on bitter almond oil, after the stilbene has passed over and solidified in scales and the heat has risen, needle-shaped crystals condense in the neck of the retort, and may be purified by boiling them in the state of fine powder with ether, which dissolves out the stilbene mixed with them. The residual white powder is boiled with a large quantity of ether, till it is completely dissolved, and the ethereal solution deposits thionessal by cooling or by spontaneous evaporation, in asbestos-like crystals grouped in tufts or spherical masses. It is however more advantageous to recrystallise the product from boiling rectified rock-oil, from which the thionessal separates on cooling in needles grouped in spherical masses.

*Properties.* Colourless, inodorous needles having a silky lustre. Melts at 148°, and solidifies on cooling, in a spongy mass, which absorbs the still liquid portion and swells up. After slow cooling, it often remains amorphous, and does not crystallise till gently heated. The vapours have a faint and not sulphurous odour.

| | | | | Laurent. |
|---|---|---|---|---|
| 26 C | 156 | 86·18 | | 86·35 |
| 9 H | 9 | 4·98 | | 4·90 |
| S | 16 | 8·84 | | 8·78 |
| $C^{26}H^{9}S$ | 181 | 100·00 | | 100·03 |

Burns with a reddish sooty flame. With bromine it immediately becomes heated, gives off vapours of hydrobromic acid and forms bromothionessal. It is but slowly attacked by boiling nitric acid, with formation of nitrothionessal; the liquid does not contain sulphuric acid. It is not decomposed by boiling alcoholic potash. Heated with potassium, it yields sulphide of potassium and a large quantity of charcoal.

It dissolves very sparingly in boiling *alcohol*, with difficulty in boiling *ether*, most abundantly in boiling *rock-oil*, from which it separates again almost completely on cooling.

## Bromothionessal. $C^{26}Br^{2}H^{7}S$.

LAURENT. *loc. cit.*

*Bromêthionessile.*

Obtained by treating thionessal with bromine. Hydrobromic acid is then evolved and a solid mass formed which may be purified by boiling with ether.

Pulverulent, melts at a high temperature, and solidifies in rhombic tables on cooling. Volatilises without decomposition.

| | | | | Laurent. |
|---|---|---|---|---|
| 26 C | 156 | 46·02 | | 49·5 |
| 7 H | 7 | 2·06 | | 2·2 |
| 2 Br | 160 | 47·20 | | |
| S | 16 | 4·72 | | |
| $C^{26}H^{7}Br^{2}S$ | 339 | 100·00 | | |

## Nitrothionessal. $C^{16}X^{2}H^{7}S$.

LAURENT. *loc. cit.*

*Nitrêthionessile.*

When thionessal is boiled for some time with nitric acid, it first softens and ultimately forms a yellow porous friable crust, which is washed with water and with alcohol, and ultimately boiled with ether,

which dissolves but little of it, and on cooling deposits it all in the form of a flocculent powder. The residue forms a pale yellow, tolerably fusible powder, which on cooling solidifies in a yellow transparent amorphous mass.

| | | | | Laurent. |
|---|---|---|---|---|
| 26 C | 156 | .... | 57·56 | 57·9 |
| 2 N | 28 | .... | 10·33 | 10·7 |
| 7 H | 7 | .... | 2·58 | 2·7 |
| S | 16 | .... | 5·91 | |
| 8 O | 64 | .... | 23·62 | |
| $C^{26}N^{2}H^{7}SO^{8}$ | 271 | .... | 100·00 | |

When heated to the boiling point, it takes fire and leaves a large quantity of charcoal. It is not attacked by potash-ley.

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## Bibenzoylimide.

$C^{28}NH^{12}O^{2} = C^{28}AdH^{11},O^{2}$.

Robson. (1851.) *Chem. Soc. Qu. J.* 4, 225; *Ann. Pharm.* 87, 122; *J. pr. Chem.* 55, 245; *Pharm. centr.* 1852, 209.

*Dibenzoylimide.*

*Formation and Preparation.* Ammoniacal gas passed into an alcoholic solution of bitter almond oil, is abundantly absorbed, and after a few hours a granular precipitate of benzoylazotide separates out, mixed with a resinous body, which is dissolved on treating the precipitate with alcohol. The residue obtained by evaporating the alcoholic solution, assumes a light red colour after several hours boiling with potash-ley, and becomes brittle and resinous. Boiling hydrochloric acid extracts from it only a small quantity of amarine, and after the residue has been treated with boiling alcohol, bibenzoylimide remains behind.

*Properties.* Yellowish powder consisting of feathery crystals.

| | | | | Robson. |
|---|---|---|---|---|
| 28 C | 168 | .... | 79·62 | 79·66 |
| N | 14 | .... | 6·60 | 6·49 |
| 13 H | 13 | .... | 6·16 | 6·43 |
| 2 O | 16 | .... | 7·62 | 7·42 |
| $C^{28}NH^{12}O^{2}$ | 211 | .... | 100·00 | 100·00 |

$(2C^{14}H^{6}O^{2} + NH^{3} = C^{28}NH^{12}O^{2} + 2HO.)$

*Decompositions.* 1. It is not altered by boiling with hydrochloric acid or potash-ley. By continued boiling with *alcoholic potash*, it yields bitter almond oil and ammonia. — 2. It is dissolved by boiling *nitric*

*acid* and crystallises out unaltered on cooling. After several hours boiling, however, it no longer crystallises, and water then throws down from the solution a body which has a strong yellow colour, is dissolved by oil of vitriol and reprecipitated therefrom by water; dissolves with yellow colour in potash or ammonia; dissolves also in hot alcohol, and separates in the crystalline form on cooling. — 3. Bibenzoylimide dissolves with fine red colour in *oil of vitriol* and is separated therefrom by water. — 4. On distilling it with *soda-lime*, a small quantity of a yellow crystalline non-azotised body sublimes, which dissolves with fine violet colour in oil of vitriol, and is insoluble in wood-spirit, alcohol and ether.

Bibenzoylimide dissolves readily in boiling *wood-spirit* and *alcohol*, but is nearly insoluble in *ether*.

## Hydrobenzamide.

$C^{42}N^2H^{16}$ (= $C^{42}AdNH^{16}$ ?)

LAURENT. (1836.) *Ann. Chim. Phys.* 62, 23; *Ann. Pharm.* 21, 130; *J. pr. Chem.* 9, 130. — *Ann. Chim. Phys.* 66, 18. — *N. Ann. Chim. Phys.* 1, 300; *Rev. scient.* 19, 48; *J. pr. Chem.* 35, 468. — *Pharm. centr.* 1836, 215; 1838, 245.
ROCHLEDER. *Ann. Pharm.* 41, 89.—*Pharm. centr.* 1842, 57.
FOWNES. *Phil. Trans.* 1845, 263; *Ann. Pharm.* 54, 363.
BERTAGNINI. *Ann. Pharm.* 88, 127.—*Pharm. centr.* 1852, 70.

*Azoture de benzène, Hydrure d'azobenzoïle, Nitrure de picramyle.*

*Formation.* By the action of ammonia on bitter almond oil (p.24).

$$3C^{14}H^6O^2 + 2NH^3 = C^{42}N^2H^{16} + 6HO.$$

*Preparation.* When the portion of rectified bitter almond oil which boils at 180° is covered with aqueous ammonia and left at rest for 14 days, $\frac{9}{10}$ of the oil solidifies in a crystalline mass. The remaining liquid is poured off, the crystals broken up, quickly shaken with a small quantity of ether to remove the adhering oil, and dissolved in boiling alcohol which leaves a small quantity of white powder undissolved; the filtered solution yields by cooling and spontaneous evaporation crystals of hydrobenzamide. (Laurent.) According to Rochleder, bitter almond oil covered with ammonia solidifies in 24 to 48 hours at ordinary temperatures, or in 6 to 8 hours after being heated to the boiling point of the ammonia, into a yellow resinous mass, which, besides hydrobenzamide, contains $\frac{1}{10}$ of a yellow-green, fetid, volatile resin; the hydrobenzamide may be purified by washing with water and crystallization from boiling alcohol.

Commercial bitter almond oil forms with aqueous ammonia a yellow resinous mass; and when this is freed by ether from adhering oil and repeatedly exhausted with boiling ether and alcohol, the decanted liquids yield several crops of crystals of hydrobenzamide, benzhydramide, azobenzoyl, a small quantity of benzoylazotide, and a substance sparingly soluble in alcohol. From this mixture the crystals of hydrobenzamide

may be picked out and purified by repeated crystallisation from alcohol. (Laurent.) When the last portion of liquid which passed over in the distillation of bitter almond oil was dissolved in 4 or 5 times its volume of alcohol, and mixed with 1 vol. hydrosulphate of ammonia, an oily mass separated, which in 24 hours solidified completely in the form of hydrobenzamide, mixed only with a few crystals of hydride of sulphobenzoyl.

Colourless rhombic octohedrons, truncated on their greater lateral edges. (Fig. 41). $a : a' = 130°$; $a : a = 122°$; $a : a'' = 84° 30'$. The crystals generally exhibit wedge-shaped elongations. (Laurent.) Tasteless; the alcoholic solution has somewhat of the taste of bitter almonds. Inodorous. Melts at 110° to a thick oil, which has a sweet taste, and after some time solidifies into an opaque brown mass.

| | | | Laurent. | Liebig. | Rochleder. |
|---|---|---|---|---|---|
| 42 C | 252 | 84·56 | 84·40 | 83·91 | 84·36 |
| 2 N | 28 | 9·40 | 9·00 | 10·01 | 9·13 |
| 18 H | 18 | 6·04 | 6·38 | 6·08 | 6·01 |
| $C^{42}N^2H^{18}$ | 298 | 100·00 | 99·78 | 100·00 | 100·00 |

*Decompositions.* 1. Hydrobenzamide when heated in the air, takes fire, and burns with a not unpleasant odour. (Laurent.) — 2. Between 120° and 130°, it changes in three or four hours into amarine. (Bertagnini.) — 3. By *dry distillation*, it yields lophine and a strong-smelling volatile oil, leaving a small quantity of carbonaceous matter. (Laurent.) — 4. When the alcoholic solution is continuously boiled, ammonia escapes, and on evaporating the alcohol, bitter almond oil remains. (Laurent, *Rev. scient.* 19, 448.) — 5. Boiled with aqueous *chromic acid*, it yields a large quantity of benzoic acid. (Fownes.) — 6. With *acids*, even at ordinary temperatures, it yields bitter almond oil and the ammonia-salt of the acid. (Laurent, Fownes.) — 7. Boiled with *potash-ley*, it changes gradually and without perceptible decrease of weight, into amarine, only a faint odour of bitter almond oil being evolved. (Fownes.) Boiled with alcoholic potash, it gives off a small quantity of ammonia and bitter almond oil. (Laurent.) — 8. When it is fused with hydrate of potash, the mass becomes first light yellow, then dark yellow, and ultimately brown and black, and if slowly heated gives off nothing but ammonia; if the heat be continued, there is given off, besides ammonia, a mixture of about 4 vol. hydrogen gas to 1 vol. carburetted hydrogen. The black residue contains carbonate of potash, cyanide of potassium, benzostilbin, benzolone, and a small quantity of a yellow oil, which thickens and becomes viscid on exposure to the air; the mass which has then become dark yellow, contains nothing but benzostilbin and a considerable quantity of the yellow oil. (Rochleder.) — 9. Heated with *potassium*, it yields a red fusible mass and a small quantity of charcoal. (Laurent.) — 10. When sulphuretted hydrogen is passed through the alcoholic solution, sulphide of stilbene is produced. (Cahours, p. 168.)

Hydrobenzamide dissolves with facility in *alcohol* and in *ether*.

*Appendix to Hydrobenzamide.*

## Benzolone. $C^{22}H^{8}O^{2}$. ?

ROCHLEDER. (1842.) *Ann. Pharm.* 41, 94.—*Pharm. Centr.* 1842, 57.

Produced, together with benzostilbin, when hydrobenzamide is strongly heated with hydrate of potash:

$$2C^{42}N^{2}H^{18} + 6HO = C^{22}H^{8}O^{2} + C^{42}H^{22}O^{4} + 4NH^{3}.$$

An intimate mixture of hydrobenzamide and hydrate of potash is heated in a silver basin till the mass assumes a black-brown colour, and the product after being rubbed to powder is treated with water, as long as the water extracts any thing from it; the residual powder is then washed on a filter with cold hydrated alcohol, till that liquid no longer assumes a yellow colour, and the residue is added to warm oil of vitriol. The blood-red solution thus formed, when gradually mixed with dilute alcohol, becomes greenish yellow and deposits small crystals of benzolone, which, if not yet sufficiently pure, must again be treated with oil of vitriol.

Small crystals which melt at 248°, and sublime almost without decomposition when strongly heated.

| | | | Rochleder. |
|---|---|---|---|
| 22 C | 132 | 84·62 | 83·50 |
| 8 H | 8 | 5·13 | 5·21 |
| 2 O | 16 | 10·25 | 11·29 |
| $C^{22}H^{8}O^{2}$ | 156 | 100·00 | 100·00 |

It is dissolved with reddish yellow colour by strong nitric acid, and precipitated therefrom by water in its original state; but fuming nitric acid converts it, with evolution of red vapours, into a yellow resin. It is not attacked by potash-ley.

Insoluble in water and alcohol.

## Benzostilbin. $C^{42}H^{22}O^{4}$.?

ROCHLEDER. (1842.) *Ann. Pharm.* 41, 93.—*Pharm. Centr.* 1841, 57.

Formed when hydrobenzamide is heated with hydrate of potash. At a strong heat, the mass blackens, and benzolone is formed at the same time.

The yellow alcoholic liquid obtained in distilling benzolone contains benzostilbin contaminated with a yellow oil which renders it more soluble. From this it may be freed: 1. By recrystallising the residue left after the evaporation of the alcohol.—2. By adding to every pound of the alcoholic liquid 8 or 10 drops of hydrochloric acid, which colours it pale red; after standing for some time however, or on boiling, it loses this colour, and at the same time, the benzostilbin separates in small crystals.

3. By passing chlorine gas into the alcoholic liquid, whereby it is immediately decolorised, becoming at the same time almost of the consistence of tar, from the presence of the separated crystals. The small crystals obtained by 2 or 3 are free from chlorine, and when immersed in ether are gradually converted into larger crystals.

Melts at 244° and sublimes at a higher temperature, for the most part decomposed.

| | | | Rochleder. |
|---|---|---|---|
| 62 C | 372 | 87·32 | 86·67 |
| 22 H | 22 | 5·17 | 5·28 |
| 4 O | 32 | 7·51 | 8·05 |
| $C^{62}H^{22}O^{4}$ | 426 | 100·00 | 100·00 |

Dissolves with pale red colour in *oil of vitriol.*
May be boiled without decomposition, with *potash-ley* of sp. gr. 1·27.
Dissolves sparingly in *alcohol.*

A mixture of benzolone and benzostilbin heated in a retort with strong potash-ley and hydrate of potash, till the mass is dry, yields a small quantity of an oil smelling deceptively like *geraniums.* (Rochleder.)

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## Amarine.

$C^{42}N^{3}H^{18} = C^{42}N^{3}H^{16},H^{2}$. ?

LAURENT. (1844.) *Compt. rend.* 19, 353; *N. J. Pharm.* 6, 178.—*Compt. chim.* 1845, 33; *J. pr. Chem.* 36, 1.—*N. Ann. Chim. Phys.* 1, 306; *Pharm. Centr.* 1845, 828.
FOWNES. *Phil. Trans.* 1845, 263; *Ann. Pharm.* 54, 363; *N. Ann. Chim. Phys.* 17, 483.
BERTAGNINI. *Ann. Pharm.* 88, 127.—*Pharm. Centr.* 1852, 70.
GÖSSMANN. *Ann. Pharm.* 93, 329.—*Pharm. Centr.* 1855, 266.

*Benzoline, Hydrure d'azobenzotline.*—Discovered at the same time by Laurent and by Fownes.

*Formation.* 1. By heating the isomeric body hydrobenzamide to between 120° and 130° (Bertagnini), or by boiling it with aqueous alkalis. (Laurent, Fownes.) — 2. By heating sulphite of benzosyl and ammonium (p. 27) with hydrate of lime. (Gössmann.)

*Preparation.* 1. When hydrobenzamide is heated for three or four hours to a temperature between 120° and 130°, the cooled vitreous mass dissolved in boiling alcohol, and hydrochloric acid added in excess, white crystals separate consisting of hydrochlorate of amarine, which may be purified by one recrystallisation from hot alcohol. (Bertagnini.) — 2. Hydrobenzamide is boiled for several hours with potash-ley; the resulting cake of resin dissolved in dilute sulphuric acid; the solution

precipitated by ammonia; and the precipitate washed with water and crystallized from hot alcohol. (Fownes.) — 3. An alcoholic solution of bitter almond oil saturated with ammoniacal gas solidifies, after 24—48 hours, into a crystalline mass composed of several substances which cannot be purified by treatment with ether. This mass is boiled with a little water to expel the greater part of the alcohol, and saturated while still hot with hydrochloric acid, whereupon an oily mass separates, and sometimes also crystals of amidobenzoic acid (p. 143). If sufficient water is present and the liquid is hot enough, the whole of the hydrochlorate of amarine remains dissolved. The liquid is decanted; any hydrochlorate of amarine that may be contained in the oil is extracted by boiling water; and the solution neutralised with ammonia, whereupon it deposits white microscopic needles of amarine, either immediately or after some minutes, according to the degree of concentration. These needles are collected on a filter, washed, dissolved in alcohol, mixed with a little hydrochloric acid; and the solution neutralised with ammonia; it then on cooling yields crystals of perfectly pure amarine. (Laurent.)

4. When a mixture of the dry sulphite of benzosyl and ammonium with three or four times its volume of very dry hydrate of lime contained in a capacious retort, is covered with a very thin layer of hydrate of lime and quickly heated over charcoal to between 180° and 200°, the neck of the retort becomes coated with an apparently amorphous mass, which, at a stronger heat, flows downwards and into the receiver, whilst needles of lophine sublime in the upper part of the neck. The amarine, part of which occupies the lower part of the neck of the retort, the rest being contained in the ammoniacal liquid in the receiver, is washed with alcohol, dissolved in alcohol mixed with hydrochloric acid, and precipitated by ammonia. Instead of the pure sulphite of benzosum and ammonium, the mass may be used which is obtained when an alcoholic solution of bitter almond oil mixed with an equivalent quantity of a saturated solution of bisulphite of ammonia, is quickly evaporated to dryness. (Gössmann.)

*Properties.* Crystallises from alcohol in shining six-sided prisms whose terminal faces are replaced by two or four faces of a rectangular octohedron. (Fig. 68, without the face *p*.) (Laurent.) Melts at 100°. (Fownes.) Solidifies on cooling in radiated rosettes (Laurent), in a vitreous transparent mass. (Fownes.) Inodorous, tasteless at first, then slightly bitter. Slightly blues red litmus paper. (Laurent.) The alcoholic solution has a strong alkaline reaction. (Fownes.) — Yields a strongly electrical powder. (Fownes.) — Introduced in small quantity (3 grains of the acetate) below the skin of dogs, rabbits, and guinea-pigs, it causes convulsions and death; when introduced into the stomach, it also produces convulsions and other morbid symptoms, but the animal recovers in a few hours. The isomeric body, hydrobenzamide does not exert any such poisonous action (Bacchetti, *Cimento*, 2, 76; *Liebig & Kopp's Jahresbericht*, 1855, 561.)

| | | | Laurent. | | Fownes. |
|---|---|---|---|---|---|
| 42 C | 252 | 84·56 | 84·66 | 84·20 | 84·22 |
| 2 N | 28 | 9·40 | 9·70 | 9·70 | 9·10 |
| 18 H | 18 | 6·04 | 6·13 | 5·97 | 6·08 |
| $C^{42}N^{2}H^{18}$ | 298 | 100·00 | 100·49 | 99·87 | 99·40 |

Isomeric with hydrobenzamide.

*Decompositions.* 1. Amarine subjected to *dry distillation*, passes over almost completely, leaving only a small residue; ammonia is evolved, an oil smelling like benzol distils over, and pyrobenzoline sublimes in the neck of the retort. (Fownes.) — 2. Amarine is briskly attacked by *bromine*, apparently with formation of hydrobromate of amarine and bromamarine; ammonia poured on the product converts it into a solid mass, the alcoholic solution of which yields crystals of amarine on cooling and deposits small radiating spherules. (Laurent.) — 3. When it is heated with aqueous *chromic acid*, a very brisk action takes place, a large quantity of benzoic acid being formed. A similar action but less violent is produced by *nitric acid*. (Fownes.) — 4. Hydrate of potash in the melted state does not act on amarine excepting at a very high temperature. (Fownes.)

*Combinations.* Amarine is insoluble in water. (Laurent, Fownes.)

The *amarine salts* are formed by direct combination. They are for the most part sparingly soluble.

*Sulphate of Amarine.* — The solution of amarine in sulphuric acid yields by spontaneous evaporation small colourless crystals resembling oxalic acid.

*Hydrochlorate of Amarine.* — When hydrochloric acid is poured upon amarine, a colourless oil is formed—formerly regarded by Laurent as isomeric with bitter almond oil and called *Hydrure de benzoïline*—which becomes more solid when dry, and may be drawn out into threads when heated. (Laurent.) Crystallises from the hot aqueous solution in small, colourless, highly lustrous needles, which effloresce in vacuo, giving off 2·4 p. c. (1 At.) water. (Fownes.) May be distilled without decomposition and passes over as an oil which solidifies without becoming opaque. (Laurent.)

| | *Dry.* | | | Fownes. | Gössmann. |
|---|---|---|---|---|---|
| 42 C | 252·0 | .... | 75·37 | 75·20 | 75·15 |
| 2 N | 28·0 | .... | 8·37 | 7·83 | |
| 19 H | 19·0 | .... | 5·68 | 5·77 | 5·62 |
| Cl | 35·4 | .... | 10·58 | 9·88 | |
| $C^{42}N^{2}H^{18},HCl$ | 334·4 | .... | 100·00 | 98·68 | |

The salt combines directly with bromine. — It is insoluble in water, but dissolves readily in alcohol and ether.

*Nitrate of Amarine.* — Amarine forms with hot dilute nitric acid a soft non-crystalline mass, which dissolves in a sufficient quantity of boiling water, and separates in microscopic crystals on cooling. (Laurent.) Small crystals having a faint lustre and remaining unaltered in vacuo; they dissolve very sparingly in water. (Fownes.)

| | | | | Fownes. |
|---|---|---|---|---|
| 42 C | 252 | .... | 69·80 | 69·70 |
| 3 N | 42 | .... | 11·64 | |
| 19 H | 19 | .... | 5·26 | 5·30 |
| 6 O | 48 | .... | 13·30 | |
| $C^{42}N^{2}H^{18},HO,NO^{5}$ | 361 | .... | 100·00 | |

With *bichloride of platinum*, hydrochlorate of amarine forms an insoluble yellowish double salt (Fownes), which contains 19·8 p. c. platinum; the formula $C^{42}N^{3}H^{18},HCl,PtCl^{2}$, requiring 19·58 p. c. (Gössmann.)

*Acetate of Amarine.* — The solution of amarine in acetic acid yields by evaporation a gummy non-crystalline mass, which dissolves very easily in water. (Fownes.)

Amarine dissolves readily in *alcohol* and *ether*.

## Ternitrohydrobenzamide.

$C^{42}N^{5}H^{15}O^{12} = C^{42}N^{2}X^{3}H^{15}$.

BERTAGNINI. (1851.) *N. Ann. Chim. Phys.* 33, 476; *Ann. Pharm.* 79, 272; *Pharm. Centr.* 1851, 68.

*Hydrobenzamide trinitrique.*

*Formation.* By the action of ammonia on nitrobenzaldide (p. 121) or sulphide of nitrobenzylene.

*Preparation.* 1. When 1 pt. of pulverised nitrobenzaldide is mixed with 5 pts. of strong ammonia, the liquid turns milky; the undissolved portion acquires a flocculent consistence, and changes in the course of 24 hours, into ternitrohydrobenzamide. If the nitrobenzaldide used in the preparation is not quite pure, the product is red-brown, but is easily purified by washing the powder with cold and digesting with lukewarm alcohol. — 2. When nitrobenzaldide is mixed with alcoholic ammonia, a solution is obtained which soon deposits resinous ternitrohydrobenzamide. — 3. When ammoniacal gas is passed over melting nitrobenzaldide, a large quantity of water is given off, and a transparent vitreous mass is formed which becomes opaque when immersed in boiling alcohol.

*Properties.* White light powder, or after fusion, a transparent vitreous mass. Separates from boiling alcohol in flakes composed of shining needles. Inodorous. Tasteless.

| | | | Bertagnini. |
|---|---|---|---|
| 42 C | 252 | 58·19 | 58·37 |
| 5 N | 70 | 16·16 | 16·27 |
| 15 H | 15 | 3·46 | 3·67 |
| 12 O | 96 | 22·19 | 21·69 |
| $C^{42}N^{5}H^{15}O^{12}$ | 433 | 100·00 | 100·00 |

*Decompositions.* 1. The compound heated to between 125° and 150°, is converted into ternitramarine. — 2. Similarly when boiled with dilute potash-ley. — 3. When boiled for some time with hydrated alcohol, it is resolved into nitrobenzaldide and ammonia. — 4. Heated with dilute acids or in contact, even at ordinary temperatures, with strong hydrochloric acid, it is converted almost instantly into nitrobenzaldide and ammoniacal salts. It dissolves easily and with rise of temperature

in cold concentrated chromic acid, the solution quickly solidifying into a crystalline mass of nitrobenzoic acid.

It is insoluble in water, very sparingly soluble in boiling alcohol, insoluble in ether and oil of turpentine.

## Ternitramarine.

$C^{42}N^{2}H^{15}O^{12} = C^{42}N^{2}X^{3}H^{13},H^{2}$. ?

BERTAGNINI. (1851.) *N. Ann. Chim. Phys.* 33, 479; *Ann. Pharm.* 79, 275.

***Amarine trinitrique.***

*Formation.* From ternitrohydrobenzamide, by heating it to between 125° and 150°, or by boiling it with aqueous potash.

*Preparation.* When ternitrohydrobenzamide is heated with a mixture of 1 measure of potash-ley of 50° Bm. and 50 measures of water, the powder cakes together and forms a brown semi-fluid mass which becomes brittle on cooling and is a mixture of ternitramarine and a brown substance. This product is dissolved in hot strong alcohol mixed with a little ether, and hydrochloric acid is added to the solution, which then immediately deposits small, white, shining needles of hydrochlorate of ternitramarine. These crystals are purified by digestion in lukewarm alcohol and decomposed by alcoholic ammonia; the alcoholic solution is evaporated; the residue freed from sal-ammoniac by washing with water, is dissolved in alcohol; and the solution is left to evaporate. — 2. Ternitrohydrobenzamide is heated in the oil-bath to between 125° and 150°, whereupon it melts into a gummy mass which becomes brittle on cooling.

Crystallises from the alcoholic solution by spontaneous evaporation in white hard nodules.

| | | | Bertagnini. |
|---|---|---|---|
| 42 C | 252 | 58·19 | |
| 5 N | 70 | 16·16 | 16·05 |
| 15 H | 15 | 3·46 | |
| 12 O | 96 | 22·19 | |
| $C^{42}N^{5}H^{15}O^{12}$ | 433 | 100·00 | |

Isomeric with ternitrohydrobenzamide.

Ternitramarine softens in boiling water and dissolves to a very slight extent, forming an alkaline solution.

The *ternitramarine salts* are very sparingly soluble in water.

*Hydrochlorate of Ternitramarine.* — Obtained by adding hydrochloric acid to the alcoholic solution of ternitramarine, which then deposits small shining needles. It is nearly insoluble in cold, sparingly soluble in strong boiling alcohol, whence it crystallises in tufts of needles on cooling.

| | | | | Bertagnini. |
|---|---|---|---|---|
| 42 C | 252·0 | 53·68 | | |
| 5 N | 70·0 | 14·91 | | 15·03 |
| 16 H | 16·0 | 3·41 | | |
| 12 O | 96·0 | 20·46 | | |
| Cl | 35·4 | 7·54 | | 7·11 |
| $C^{42}N^{5}H^{15}O^{12},HCl$ | 469·4 | 100·00 | | |

*Nitrate of Ternitramarine* crystallises in needles from boiling alcohol. It is insoluble in water.

*Mercuric Chloride* forms with an alcoholic solution of ternitramarine a somewhat crystalline precipitate; *bichloride of platinum* forms small heavy yellow nodules insoluble in alcohol.

Ternitramarine dissolves sparingly in strong boiling *alcohol*, the dissolved portion separating in the amorphous state on cooling. It dissolves pretty readily in *ether*, very easily in a mixture of *ether* and *alcohol*.

## Lophine.

$C^{46}N^{2}H^{15}$ or $C^{44}N^{2}H^{16}$.

LAURENT. (1844.) *Rev. scient.* 18, 272; *J. pr. Chem.* 35, 455.—*N. Ann. Chim. Phys.* 19, 369; *Compt. rend.* 20, 1117; *Ann. Pharm.* 62, 103; *J. pr. Chem.* 40, 407; *Pharm. Centr.* 1844, 335; 1847, 383.
GÖSSMANN. *Ann. Pharm.* 93, 331; *Pharm. Centr.* 1855, 266.
GÖSSMANN & ATKINSON. *Ann. Pharm.* 97, 283; *Chem. Soc. Qu. J.* 9, 220.

*Lophin, Lophyle.*

*Formation.* 1. By the dry distillation of hydrobenzamide, benzoylazotide or azosulphide of benzylene. (Laurent.)—2. By heating sulphite of benzosyl and ammonium with hydrate of lime. (Gössmann.)

*Preparation.* 1. When hydrobenzamide is heated, ammonia escapes together with a mobile fragrant oil [benzol? L.], and there remains a fused mass which may be distilled at a high temperature, but is more advantageously treated by pouring it out, pulverising it when cold, and digesting it in hot ether, which extracts a small quantity of a body crystallising in shining laminæ as the solution cools. The residue is heated with alcohol to the boiling point, and hot caustic potash added to it till the whole is dissolved; the liquid on cooling deposits threadlike crystals which may be washed with alcohol. It is better however to boil the residue insoluble in ether with alcohol containing hydrochloric acid, mix the solution at the boiling heat with ammonia, and leave it to cool. (Laurent.)—2. From the mixture of lophine and amarine obtained by distilling benzoylazotide, the amarine is extracted by boiling with rock-oil, or the lophine by boiling with alcohol containing hydrochloric acid. (Laurent.)—3. From the distillate obtained by heating azosulphide of benzylene, the oily products are extracted by ether, the stilbene by boiling alcohol, and the thionessal by rock-oil, and the residue consisting of lophine is dissolved by boiling with alcohol and potash or with alcohol containing hydrochloric acid. A similar process is adopted with

the product resulting from distilling the mixture obtained by treating bitter almond oil for two or three weeks with hydrosulphate of ammonia, which mixture also contains picril. (Laurent.) — 4. The needle-shaped crystals (p. 195) which sublime in the neck of the retort during the distillation of sulphite of benzosyl and ammonium with hydrate of lime, are dissolved in hot alcohol and recrystallised after being treated with animal charcoal. The formation of the lophine is facilitated by heating the retort very quickly and covering the upper part at the commencement of the distillation with red-hot coals (Gössmann). ¶ The best mode of conducting the process is to add a quantity of quick lime equal in weight to the hydrate, introduce the mixture into a rather shallow globular retort coated with clay, and cover the retort as far it is filled with the mixture, with live coals, from the very beginning of the operation. Only small quantities should be operated on at once, from 10 to 15 grammes of the sulphite with about four to six times the quantity of the lime-mixture. When the operation is thus conducted, only a small quantity of amarine forms at first, and when this has melted down, the upper part of the retort begins to be covered with radiant masses of lophine, and the formation of secondary products ceases, nothing being formed but lophine and free ammonia. At the commencement, a small quantity of an aromatic oil accompanies the lophine, apparently resulting from the decomposition of the amarine into lophine and other products, the principal of which is amarone. (Gössmann & Atkinson.) Purification as in Laurent's method (1).

*Properties.* Colourless needles often an inch long, grouped in tufts and having a lustre similar to that of caffeine; they become opalescent after a while but retain their lustre. At 250°, the compound sublimes gradually but completely, without previous fusion and without decomposition. It melts at 265°, forming a transparent liquid which at 260° solidifies in a radiating crystalline mass. Tasteless and inodorous, with scarcely any alkaline reaction. The alcoholic solution exhibits fluorescence like quinine, but not in so high a degree. No action upon polarised light. (Gössmann & Atkinson.) ¶.

| Calculation I. | | | Calculation II. | | |
|---|---|---|---|---|---|
| 46 C | 276 | 86·25 | 44 C | 264 | 85·72 |
| 2 N | 28 | 8·75 | 2 N | 28 | 9·09 |
| 16 H | 16 | 5·00 | 16 H | 16 | 5·19 |
| $C^{46}N^{2}H^{16}$ | 320 | 100·00 | $C^{44}N^{2}H^{16}$ | 308 | 100·00 |

Calculation III.

| | | |
|---|---|---|
| 42 C | 252 | 84·84 |
| 2 N | 28 | 5·73 |
| 17 H | 17 | 9·43 |
| $C^{42}N^{2}H^{17}$ | 297 | 100·00 |

*Analyses.*

| | Laurent. *a.* | Laurent. *b.* | Gössmann. | Gössmann & Atkinson. *mean.* |
|---|---|---|---|---|
| C | 85·59 | 86·05 | 85·69 | 84·73 |
| N | 9·24 | 8·83 | | 9·47 |
| H | 5·38 | 5·12 | 5·50 | 5·63 |
| | 100·21 | 100·00 | | 99·83 |

Laurent first proposed the formula $C^{46}N^2H^{17}$, for which he afterwards substituted $C^{46}N^2H^{16}$. Gerhardt (*Traité*, 3, 139) regarded lophine as identical with Fownes's pyrobenzoline $C^{42}N^2H^{16}$ (p. 204). Gössmann (*Ann. Pharm.* 93, 331) adopted Laurent's earlier formula.—Calculation II agrees better with some of the analyses of lophine and its compounds, and explains the formation of lophine from hydrobenzamide simply according to the equation:

$$4C^{42}N^2H^{18} = 3C^{46}N^2H^{16} + 3C^{12}H^6 + 2NH^3 \text{ [L.]}.$$

[Gössmann & Atkinson suggest that the discrepancies between the several analyses of lophine may arise from the presence of small quantities of amarone (p. 208) in some of the preparations analysed. They regard lophine as identical with pyrobenzoline, and propose a formula differing from the double of Fownes's original formula ($C^{21}NH^9$) by only 1 At. hydrogen. The formula $C^{42}N^2H^{17}$ is however somewhat improbable on account of the uneven number of hydrogen-atoms. The correct formula is more probably $C^{42}N^2H^{16}$ (W.)].

*Decompositions.* Lophine boiled with nitric acid forms nitrolophine. (Laurent.) It is dissolved by bromine without evolution of vapours of hydrobromic acid. When the mass is dissolved in ether and the solution mixed with alcohol and abandoned to spontaneous evaporation, beautiful yellow prisms with rectangular base separate out; these crystals give off bromine when heated, and when water is poured upon them, turn white and fall to powder. (Laurent.) Lophine in contact with iodide of ethyl does not form any substitution compound, not even when the two bodies are heated together to 100° in a sealed tube for several weeks. A portion of the iodide of ethyl is decomposed into alcohol and hydriodic acid, which combines with the lophine. (Gössmann & Atkinson.)

*Combinations.* Lophine does not dissolve in water.

It dissolves with the greatest facility and without decomposition in boiling alcoholic potash. (Laurent.)

The *lophine-salts* are for the most part insoluble in water, and sparingly soluble in alcohol. — They are rather instable, having a tendency when recrystallised to give up part of their acid and form basic compounds; this is particularly the case with the sulphate. (Gössmann & Atkinson.)

*Sulphate of Lophine.* — Lophine is heated with alcohol, with addition of sulphuric acid, and the solution mixed with hot water, whereupon crystallisation ensues. — Small shining rectangular laminæ. The alcoholic solution reddens litmus and is precipitated by water, a portion however remaining in solution, so that on adding ammonia, a precipitate of lophine is still obtained. Laurent found in the dry salt 11·5 and 13·2 per cent. of sulphuric acid; the neutral salt requires 11·21 per cent. of sulphuric acid. (Laurent.) — ¶ When a solution of lophine to which excess of sulphuric acid has been added is left to evaporate slowly, the sulphate separates in broad transparent tables which become opaque and effloresce on exposure to the air. When crystallised more rapidly, the compound separates in large needles, which, if left for some time in the mother-liquor, change into small white opaque needles. At each crystallisation, the salt becomes more basic, and by frequent solution and recrystallisation, the acid may be almost entirely removed. (Gössmann & Atkinson.)

*Hydriodate of Lophine.* — Prepared like the hydrochlorate. Crystallises readily in large needles, which are more soluble in alcohol and ether

than the hydrochlorate. From a very acid solution, it separates in granular crystals. It dissolves very easily in iodide of ethyl. In other respects it resembles the hydrochlorate. (Gössmann & Atkinson.) ¶.

*Hydrochlorate of Lophine.* — Separates quickly on cooling from a solution of lophine in boiling alcohol containing hydrochloric acid. If a solution in a sufficient quantity of boiling alcohol be mixed with such a quantity of hot water that no immediate precipitate is formed, the liquid on cooling yields well defined crystalline laminæ. (Laurent.) — ¶. When hydrochloric acid is added to a hot saturated alcoholic solution of lophine till the mixture exhibits a decided acid reaction, the hydrochlorate separates on cooling in large transparent needles very much like the crystals of pure lophine. If left for some time in the mother-liquor, they change into small white opaque prisms, an alteration which is probably due to loss of water. Several other lophine compounds exhibit a similar change. When lophine is treated with strong hydrochloric acid, it becomes resinous, and can only be restored to the crystalline state by removing the acid and crystallising from alcohol. (Gössmann & Atkinson.) Nearly insoluble in water, but dissolves pretty easily in alcohol. (Laurent.) — ¶. Has a slight acid reaction. Dissolves more readily in water and alcohol than the pure base, and exhibits stronger fluorescence. (Gössmann & Atkinson.) ¶.

| Calculation I. | | | | Calculation II. | | | | Laurent. |
|---|---|---|---|---|---|---|---|---|
| $C^{46}N^{2}H^{16}$ | 320·0 | | 89·79 | $C^{44}N^{2}H^{16}$ | 308·0 | | 89·43 | |
| ClH | 36·4 | | 10·21 | ClH | 36·4 | | 10·57 | 10·25 |
| $C^{46}N^{2}H^{16}$,ClH | 356·4 | | 100·00 | $C^{44}N^{2}H^{16}$,ClH | 344·4 | | 100·00 | |

| Calculation III. | | | | Gössmann & Atkinson. |
|---|---|---|---|---|
| 42 C | 252·0 | | 73·57 | 73·79 |
| 2 N | 28·0 | | 8·17 | |
| 19 H | 19·0 | | 5·54 | 5·58 |
| Cl | 35·4 | | 10·36 | 9·42 |
| O | 16 0 | | 2·36 | |
| $C^{42}N^{2}H^{17}$,HCl + Aq | 350·4 | | 100·00 | |

*Nitrate of Lophine.* — Fine light laminæ, devoid of lustre. When heated till they soften, they give off 2 At. water. (Laurent.) — From a concentrated alcoholic solution of lophine acidulated with nitric acid, the salt crystallises in small plates which if covered with strong nitric acid which is free from nitrous acid, are converted into an oily mass. (Gössmann & Atkinson.)

| I. | *Anhydrous.* | | | II. | *Anhydrous.* | | | Laurent. |
|---|---|---|---|---|---|---|---|---|
| 46 C | 276 | | 72·07 | 44 C | 264 | | 71·17 | 71·00 |
| 3 N | 42 | | 10·96 | 3 N | 42 | | 11·32 | |
| 17 H | 17 | | 4·44 | 17 H | 17 | | 4·58 | 4·70 |
| 6 O | 48 | | 12·53 | 6 O | 48 | | 12·93 | |
| $C^{46}N^{2}H^{16}$,$NO^{6}H$ | 383 | | 100·00 | $C^{44}N^{2}H^{16}$,$NO^{6}H^{5}$ | 371 | | 100·00 | |

| I. | *Crystallised.* | | | II. | *Crystallised.* | | | Laurent. |
|---|---|---|---|---|---|---|---|---|
| 46 C | 276 | | 68·82 | 44 C | 264 | | 67·86 | 67·60 |
| 3 N | 42 | | 10·48 | 3 N | 42 | | 10·79 | 10·80 |
| 19 H | 19 | | 4·74 | 19 H | 19 | | 4·88 | 4·95 |
| 8 O | 64 | | 15·96 | 8 O | 67 | | 16·47 | 16·65 |
| $C^{46}N^{2}H^{16}$,$NO^{6}H$ + 2Aq | 401 | | 100·00 | $C^{44}N^{2}H^{16}$,$NO^{6}H$ + 2Aq | 389 | | 100·00 | 100·00 |

When heated to complete fusion, it swells up, gives off red vapours and perhaps also a little water. The residue contains 78·5 p. c. C, 8·5 N, 5·0 H, and 8·0 O, which is nearly the composition of 1 At. lophine *minus* 1 At. nitric oxide; it is perhaps only a mixture. (Laurent.)

¶. *Lophine with Nitrate of Silver.* — *a.* $C^{42}N^2H^{17},NO^6Ag$. — When a neutral, moderately concentrated alcoholic solution of nitrate of silver is mixed with a hot saturated alcoholic solution of lophine, the mixture solidifies on cooling, in a mass of crystals; and on dissolving these in cold alcohol and leaving the solution to evaporate, the compound *a* separates in tolerably large white needles. — *b.* $2C^{42}N^2H^{17},3NO^6Ag$. — On attempting to purify the compound *a* by recrystallisation, it changes by boiling into a pulverulent, crystalline, sparingly soluble substance which settles down with a slight violet tint. It contains 29·01 p. c. silver, the formula *b* requiring 29·36 p. c. — *c.* $2C^{42}N^2H^{17},NO^6Ag$. Separates in brilliant white needles, after the compound *b* has been removed and the solution further evaporated. Contains 13·92 p. c. the calculated quantity being 14·14 p. c. The change produced in *a* by boiling is represented by the equation:

$$4(C^{42}N^2H^{17},NO^6Ag) = 2C^{42}N^2H^{17},3NO^6Ag + 2C^{42}N^2H^{17},NO^6Ag.$$

(Gössmann & Atkinson.) — [A similar equation will of course hold good if lophine be regarded as $C^{41}N^2H^{16}$. On this hypothesis also the compound *b* should contain 29·40 p. c. and *c* should contain 14·17 p. c. silver,] ¶.

*Lophine with Bichloride of Platinum.* — $4C^{42}N^2H^{17},3PtCl^2$ — When a concentrated alcoholic solution of lophine is mixed with a concentrated neutral alcoholic solution of bichloride of platinum, a compound separates in clear, orange-yellow, microscopic crystals containing 17·38 p. c. platinum. The above formula requires 17·45 p. c. (Gössmann & Atkinson.) ¶.

*Chloroplatinate of Lophine.* — When solutions of hydrochlorate of lophine and bichloride of platinum in boiling alcohol are mixed together, the platinum-salt crystallises in a few hours, provided the solution is not too strong, in long, pale orange-coloured rhombic tables, which may be washed with cold alcohol. (Laurent.) — On mixing a dilute alcoholic solution of bichloride of platinum with a warm moderately concentrated solution of lophine containing excess of hydrochloric acid, crystals which are often needle-shaped, separate as the liquid cools, and sometimes after a while crumble to a crystalline powder of a fine orange-colour. This salt is more soluble in alcohol than any other compound of lophine. (Gössmann & Atkinson.)

| Calculation I. | | | Calculation II. | | |
|---|---|---|---|---|---|
| 46 C | 276·0 | 52·46 | 44 C | 264·0 | 51·34 |
| 2 N | 28·0 | 5·32 | 2 N | 28·0 | 5·44 |
| 17 H | 17·0 | 3·23 | 17 H | 17·0 | 3·32 |
| 3 Cl | 106·2 | 20·18 | 3 Cl | 106·2 | 20·65 |
| Pt | 99·0 | 18·81 | Pt | 99·0 | 19·25 |
| $C^{46}N^2H^{16},HCl,PtCl^2$ | 526·2 | 100·00 | $C^{44}N^2H^{16},HCl,PtCl^2$ | 514·2 | 100·00 |

Calculation III.

| | | |
|---|---|---|
| 42 C | 252·0 | 50·08 |
| 2 N | 28·0 | 3·58 |
| 18 H | 18·0 | 5·56 |
| 3 Cl | 106·2 | 21·16 |
| Pt | 99·0 | 19·62 |
| $C^{42}N^2H^{17},HCl,PtCl^2$ | 503·2 | 100·00 |

*Analyses.*

| | Laurent. | Gössmann. | Gössmann & Atkinson. |
|---|---|---|---|
| C | | | 49·22 |
| H | | | 3·95 |
| Cl | 19·73 | | |
| Pt | 18·25 | 18·89 | 19·77 |

If an alcoholic solution of lophine be heated for some time with excess of bichloride of platinum, the base becomes essentially altered; platinum separates out in a state of very fine division, and the filtered liquid is very difficult to crystallise. The body which separates out is generally very soft, adhering together in a resinous mass, and the quantity of platinum in it is less than in the crystallised double salt. (Gössmann & Atkinson.)

Lophine dissolves very sparingly in boiling *alcohol* and in *ether*, and crystallises in needles as the solution cools. It dissolves to about the same amount in *rock-oil* and oil of *turpentine*, whence it separates on cooling in the form of a white crystalline powder. (Laurent.)

*Appendix to Lophine.*

## Pyrobenzoline. $C^{42}N^{2}H^{16}$.

Fownes. (1845.) *Ann. Pharm.* 54, 365 and 368.

Passes over, together with an oil, in the distillation of amarine, and crystallises in the neck of the retort. It may be freed from oil by pressure between bibulous paper and then crystallised from boiling alcohol.

Melts when heated and sublimes, even below its boiling point, in feathery crystals resembling those of benzoic acid. The fused mass solidifies in a radiated crystalline mass on cooling. Tasteless. The alcoholic solution has little or no alkaline reaction.

| | | | Fownes. |
|---|---|---|---|
| 42 C | 252 | 85·13 | 84·94 |
| 2 N | 28 | 9·46 | 9·11 |
| 16 H | 16 | 5·41 | 5·43 |
| $C^{42}N^{2}H^{16}$ | 296 | 100·00 | 99·48 |

Most probably identical with lophine.

Insoluble in water, acids, or alkalis.

Dissolves sparingly in cold, readily in hot *alcohol*.

## Nitrolophine.

LAURENT. (1844.) *Rev. scient.* 18, 272; *J. pr. Chem.* 35, 450.

*Nitrolophyle.*

Lophine boiled with nitric acid forms a yellow oil which solidifies on cooling and may be purified.

Orange-yellow crystalline powder. Melts when heated and appears to volatilise partly undecomposed, then suddenly becomes red hot and leaves a large quantity of charcoal.

| I. | *Anhydrous.* | | | II. | *Anhydrous.* | | | Laurent. |
|---|---|---|---|---|---|---|---|---|
| 46 C | 276 | .... | 60·66 | 44 C | 264 | .... | 59·59 | .... 60·00 |
| 5 N | 70 | .... | 15·38 | 5 N | 70 | .... | 15·80 | .... 15·70 |
| 13 H | 13 | .... | 2·86 | 13 H | 13 | .... | 2·93 | .... 3·14 |
| 12 O | 96 | .... | 21·10 | 12 O | 96 | .... | 21·68 | .... 21·16 |
| $C^{46}X^{3}N^{3}H^{13}$ | 455 | .... | 100·00 | $C^{44}X^{3}N^{3}H^{13}$ | 443 | .... | 100·00 | .... 100·00 |

| I. | *In vacuo.* | | | II. | *In vacuo.* | | | Laurent. |
|---|---|---|---|---|---|---|---|---|
| 46 C | 276 | .... | 56·22 | 44 C | 264 | .... | 55·12 | .... 55·0 |
| 5 N | 70 | .... | 14·25 | 5 N | 70 | .... | 14·61 | .... 14·8 |
| 17 H | 17 | .... | 3·46 | 17 H | 17 | .... | 3·55 | .... 3·4 |
| 16 O | 128 | .... | 26·07 | 16 O | 128 | .... | 26·72 | .... 26·8 |
| $C^{46}X^{3}N^{3}H^{13}$ + 2Aq | 491 | .... | 100·00 | $C^{44}X^{3}N^{3}H^{13}$ + 4Aq | 479 | .... | 100·00 | .... 100·0 |

Nitrolophine dissolves in caustic potash, forming a mahogany-coloured solution, which, when mixed with water yields a reddish precipitate turning yellow in washing; the wash-water when boiled again yields a yellow precipitate. Both precipitates appear to consist of unaltered nitrolophine.

It dissolves very sparingly in boiling alcohol, and the solution on cooling deposits flakes which under the microscope appear to consist of aggregated laminæ.

## Azobenzoilide. $C^{84}N^{5}H^{28}$.

LAURENT. (1844.) *N. Ann. Chim. Phys.* 1, 304.—*Ann. Pharm.* 38, 331.—*Pharm. centr.* 1841, 501.

*Azoture d'azostilbase.*

Bitter almond oil was shaken up with potash and chloride of iron, and the first $\frac{1}{8}$ which passed over was covered with an equal volume of ammonia. It then after a few days deposited a crystalline substance, and in three weeks half of the oil solidified. Ether extracted the rest of the oil and left azobenzoilide.

Dull white powder composed of microscopic rhombic or irregular six-sided prisms. Inodorous. Solidifies after fusion, and forms an opaque mass, which, under the microscope, exhibits rhombic figures with two, and six-sided figures with three diagonals.

| | | | Laurent. |
|---|---|---|---|
| 84 C | 504 | 83 03 | 83·0 |
| 5 N | 70 | 11·53 | 12·0 |
| 33 H | 33 | 5·44 | 5·6 |
| $C^{84}N^{5}H^{33}$ | 607 | 100·00 | 100·0 |

Isomeric with azobenzoide and azobenzoidine (Laurent). Its relation to bitter almond oil and ammonia is expressed by the equation:

$$6C^{14}H^{6}O^{2} + 5NH^{3} = C^{84}N^{5}H^{3} + 12HO + 6H \text{ [L.]}.$$

Appears to be altered by continued fusion, inasmuch as the cooled mass crystallises less distinctly and forms only a few rhombic prisms with a black rhombic spot in the centre; it remains soft after cooling. — It dissolves in hot nitric acid without evolution of red vapours; and the solution on cooling, yields microscopic four-sided prisms with dihedral summits; which appear to be undecomposed azobenzoilide. — With boiling sulphuric acid it forms a yellow solution, in which ammonia produces a white precipitate.

It is insoluble in alcohol, and very sparingly soluble in ether.

## Benzoylazotide.

$$C^{30}N^{2}H^{12} = C^{28}C_{v}AdH^{13}. ?$$

LAURENT. (1837.) *Ann. Chim. Phys.* 66, 187; *Pharm. Centr.* 1838, 294. — *Rev. scient.* 18, 207; *J. pr. Chem.* 35, 483. — *Rev. scient.* 19, 447.

LAURENT & GERHARDT. *Compt. chim.* 1850, 113; *Compt. rend.* 30, 404.

ROBSON. *Chem. Soc. Qu. J.* 4, 225; *Ann. Pharm.* 81, 127; *Pharm. Centr.* 1852, 209.

*Formation.* By the action of ammonia on bitter almond oil containing prussic acid:

$$2C^{14}H^{6}O^{2} + NH^{3} + C^{2}NH = C^{30}N^{2}H^{12} + 4HO.$$

Frequently produced by the action of hydrosulphate of ammonia on bitter almond oil, either with or without thiobenzaldin.

*Preparation.* 1. The yellow resinous mixture obtained from bitter almond oil which has stood for four weeks in contact with an equal volume of ammonia (p. 25), is treated with boiling ether, which dissolves hydrobenzamide, benzhydramide, a less soluble body, and a small quantity of azobenzoyl, whilst a mixture of azobenzoyl and benzoylazotide remains undissolved. This mixture is boiled with alcohol, which dissolves

out the azobenzoyl and a small quantity of the benzoylazotide, and the residue is recrystallised from boiling alcohol. (Laurent.) — 2. When bitter almond oil saturated at 100° with dry ammoniacal gas, is dissolved in a mixture of ether and alcohol, a crystalline deposit forms in the course of 24 hours and continues to increase for three or four days. On treating this deposit with boiling alcohol, benzoylazotide remains behind. (Laurent & Gerhardt.) — 3. The mixture of benzoylazotide and bibenzoylamide produced by passing ammoniacal gas into an alcoholic solution of bitter almond oil (p. 25) is treated with alcohol which dissolves the bibenzoylamide. (Robson.)

*Properties.* White crystalline powder composed of microscopic short right rhombic prisms entirely without modification. Melts when heated and solidifies on cooling in a vitreous mass, in which a few oblique prisms separate. Inodorous; tasteless.

| | | | Laurent. | Laurent & Gerhardt. | Robson. |
|---|---|---|---|---|---|
| 30 C | 180 | 81·81 | 81·77 | 81·55 | 81·21 |
| 2 N | 28 | 12·77 | 13·08 | 12·90 | |
| 12 H | 12 | 5·42 | 5·10 | 5·37 | 5·55 |
| $C^{30}N^2H^{12}$ | 220 | 100·00 | 99·95 | 99·82 | |

When rather strongly heated, it gives off an oil, afterwards a sublimate of lophine and amarone, and ultimately leaves a carbonaceous residue. (Laurent.)

When immersed in strong potash-ley, it is gradually converted into rhombic prisms and other products. (Laurent.)

When boiled with alcohol containing hydrochloric acid, it gives off hydrocyanic acid. (Laurent & Gerhardt; Robson.)

It is insoluble in water.

It dissolves in 300—400 pts. of *alcohol*, but is insoluble in ether.

## Quadrat's Compound resembling Benzoylazotide.

*Ann. Pharm.* 71, 18.

*Formation.* By heating sulphocyanobenzylene (p. 163).

$$2C^{16}NH^5S^2 = C^{30}N^2H^{10} + 2CS^2. ?$$

*Preparation.* The resinous mass produced by heating sulphocyanobenzylene is exhausted with alcohol and the needles forming the residue are washed with alcohol (p. 163).

*Properties.* Slender needles, permanent at 100°.

| | | | Quadrat. |
|---|---|---|---|
| 30 C | 180 | 82·57 | 82·53 |
| 2 N | 28 | 12·85 | 12·53 |
| 10 H | 10 | 4·59 | 5·26 |
| $C^{30}N^2H^{10}$ | 228 | 100·01 | 100·32 |

The compound is not decomposed by nitric acid.

It is insoluble in water and very sparingly soluble in alcohol.

## Amarone. $C^{32}NH^{11}$.

LAURENT. (1845.) *Rev. scient.* 18, 207; *J. pr. Chem.* 35, 453; *Compt. rend.* 18, 1016.

*Formation and Preparation.* The substance which sublimes in the neck of the retort when benzoylazotide is heated (p. 207), is freed from adhering oil by treatment with ether, and boiled with alcohol containing hydrochloric acid to dissolve lophine; the residue is washed with alcohol, dried, and dissolved in boiling rock-oil; and the needles which crystallise on cooling are washed with ether.

*Properties.* Small colourless needles. Inodorous. Melts at 233°, and solidifies in a radiating mass on cooling.

| | | | | Laurent. |
|---|---|---|---|---|
| 32 C | 192 | | 88·46 | 88·36 |
| N | 14 | | 6·47 | |
| 11 H | 11 | | 5·07 | 5·16 |
| $C^{32}NH^{11}$ | 217 | | 100·00 | |

Amarone is not decomposed by boiling with alcoholic potash.

It is insoluble in water.

It dissolves in oil of vitriol, with a splendid blood-red colour which immediately disappears on addition of water: a concentrated solution in hot oil of vitriol deposits crystals of amarone in proportion as it absorbs moisture from the air.

It dissolves sparingly in boiling nitric acid and solidifies in shining needles on cooling.

It dissolves very sparingly in alcohol, somewhat more readily in ether.

## Azobenzoyl. $C^{42}N^{2}H^{16}$.

LAURENT. (1837.) *Ann. Chim. Phys.* 66, 185; *Pharm. Centr.* 1838, 294.

*Formation.* By treating bitter almond oil containing hydrocyanic acid with ammonia (p. 25).

*Preparation.* The alcohol which has been used to separate benzoylazotide (p. 206), from the admixed azobenzoyl, is evaporated, the residue again boiled with alcohol, and so forth, till the crystals of azobenzoyl are no longer mixed with benzoylazotide.

*Properties.* White shining powder resembling starch, and consisting of very small smooth oblique rhombic tables or somewhat elongated

irregular six-sided tables. Inodorous. Melts when heated, forming a thick liquid which solidifies to a transparent gum on cooling.

| I. | | | | II. | | | | Laurent. |
|---|---|---|---|---|---|---|---|---|
| 42 C | 252 | .... | 85·42 | 44 C | 264 | .... | 85·71 | .... 85·24 |
| 2 N | 28 | .... | 9·49 | 2 N | 28 | .... | 9·09 | |
| 15 H | 15 | .... | 5·09 | 16 H | 16 | .... | 5·20 | .... 5·23 |
| $C^{42}N^2H^{15}$ | 295 | .... | 100·00 | $C^{44}N^2H^{16}$ | 308 | .... | 100·00 | |

Laurent's formula I, affords no explanation of the formation of azobenzoyl; according to II, its formation is represented by the equation:

$$3C^{14}H^6O^2 + NH^3 + HCy = C^{44}N^2H^{16} + 6HO.$$

and the compound should perhaps be regarded as $C^{42}CyNH^{16}$ [L.].

Azobenzoyl is decomposed at a high temperature into an oil, a solid body, and charcoal.

When boiled with alcohol containing hydrochloric acid, it gives off hydrocyanic acid. (Laurent & Gerhardt, *Compt. chim.* 1850, 113.)

It is insoluble in water.

It dissolves in more than 300 pts. of boiling *alcohol*, much more readily in *ether*.

## Benzhydramide.

$$C^{44}N^2H^{18}O^2 = C^{42}CyAdH^{16},O^2. ?$$

LAURENT. *Ann. Chim. Phys.* 66, 184; *Pharm. Centr.* 1838, 294.
LAURENT & GERHARDT. *Comp. chim.* 1850, 114; *Compt. rend.* 30, 404.

*Formation.* By the action of ammonia on crude bitter almond oil. (Laurent.) By the action of cyanide of ammonium on pure bitter almond oil. (Laurent & Gerhardt):

$$3C^{14}H^6O^2 + NH^3 + C^2NH = C^{44}NH^{18}O^2 + 4HO.$$

*Preparation.* The yellow resinous mass obtained by the action of ammonia on commercial bitter almond oil is repeatedly boiled with alcohol or ether, and from the crystalline mixture which the liquid deposits on cooling, the crystals of benzhydramide are selected by the aid of the microscope (pp. 25, 191). They are difficult to separate from another substance which crystallises in needles. (Laurent.) — 2. The hot alcoholic solution obtained in Laurent & Gerhardt's preparation of benzoylazotide (p. 206), deposits by cooling and spontaneous evaporation, small needles mixed with drops of oil; they must be quickly washed with a small quantity of ether-alcohol, and recrystallised from hot alcohol. (Laurent & Gerhardt.)

*Properties.* Colourless, microscopic, rectangular prisms with two terminal faces intersecting at an obtuse angle. (Laurent & Gerhardt.)

Sometimes two lateral edges are truncated, so that six-sided prisms are produced. (Laurent.) Melts without decomposition and solidifies in a resinous mass on cooling.

| | | | Laurent. | Laurent & Gerhardt. |
|---|---|---|---|---|
| 44 C | 264 | 80·98 | 83·84 | 80·27 |
| 2 N | 28 | 8·59 | 8·90 | 9·50 |
| 18 H | 18 | 5·52 | 6·16 | 5·41 |
| 2 O | 16 | 4·91 | 1·10 | 4·82 |
| $C^{44}N^{2}H^{18}O^{2}$ | 326 | 100·00 | 100·00 | 100·00 |

Laurent, from his own analysis, which, according to Laurent & Gerhardt, was probably made with an impure substance, deduced the formula $C^{42}N^{2}H^{18}$, according to which benzhydramide should be isomeric with hydrobenzamide.

*Decompositions.* 1. Benzhydramide heated above its melting point gives off a strong odour of hydrocyanic acid, and yields an oil, a crystalline sublimate, and a small quantity of charcoal. (Laurent; Laurent & Gerhardt.) — 2. It is not decomposed by cold hydrochloric acid. (Laurent.) Boiled with alcohol containing hydrochloric acid, it yields hydrocyanic acid and sal-ammoniac. (Laurent & Gerhardt.)

It is insoluble in water, sparingly soluble in cold, more readily in hot *alcohol*, very readily in *ether*.

*Appendix to Benzhydramide.*

## Benzamil.

LAURENT. (1845.) *Rev. scient.* 19, 446; *J. pr. Chem.* 35, 467.

Obtained as follows: Bitter almond oil, after being shaken up with potash, was distilled till about $\frac{2}{3}$ had passed over; the residue dissolved in ether-alcohol; ammoniacal gas passed into the solution; and the resulting deposit was separated from the supernatant liquid, and boiled with a large quantity of ether. The solution on cooling became filled with delicate silky crystals, and on addition to these, benzamil was obtained in the form of a white powder.

Benzamil separates from its solution in a very large quantity of hot ether, in the form of a white powder consisting of microscopic right rhombic prisms, having their terminal faces replaced by two faces which rest on the acute lateral edges. Melts at 170°, and after cooling remains for a long time in the form of a liquid paste.

| | | | Laurent. |
|---|---|---|---|
| 56 C | 336 | 80·7 | 80·4 |
| 20 H | 20 | 6·7 | 6·6 |
| 2 N | 28 | 4·8 | 4·9 |
| 4 O | 32 | 7·8 | 8·1 |
| $C^{56}H^{20}N^{2}O^{4}$ | 416 | 100·0 | 100·0 |

According to Laurent, the substance analysed was not quite pure.

*Decompositions.* Benzamil distils apparently without alteration, but the distillate is easily soluble in ether. With nitric acid it forms an oil which crystallises on cooling. It is decomposed by boiling with hydrochloric acid or alcohol; a small quantity of white powder then remaining. It is readily dissolved by alcoholic potash, and the liquid on cooling deposits a crystalline body.

It is nearly insoluble in alcohol, ether and rock-oil, even at the boiling heat.

## Azobenzoide. $C^{86}N^5H^{37}$. ?

LAURENT. (1837.) *Ann. Chim. Phys.* 66, 190; *Pharm. Centr.* 1838, 295.

*Formation and Preparation.* By the action of ammonia on bitter almond oil (p. 25).

*Properties.* White powder, which does not exhibit any crystalline structure when examined by the microscope. After fusion, it solidifies in crystalline granules.

| I. | | | | II. | | | | Laurent. |
|---|---|---|---|---|---|---|---|---|
| 84 C | 504 | | 83·03 | 86 C | 516 | | 82·82 | 82·96 |
| 5 N | 70 | | 11·53 | 5 N | 70 | | 11·24 | 11·76 |
| 33 H | 33 | | 5·44 | 37 H | 37 | | 5·94 | 5·60 |
| $C^{84}N^5H^{33}$ | 607 | | 100·00 | $C^{86}N^5H^{37}$ | 623 | | 100·00 | 100·32 |

Isomeric with azobenzoidin, and according to Laurent (I) with azobenzoilide. If azobenzoide and azobenzoidin, as supposed by Laurent & Gerhardt (*Compt. chim.* 1850, 113), owe their origin to the action of prussic acid, their formation may be most simply expressed by the equation:

$$6C^{14}H^6O^2 + 4NH^3 + CyH = C^{86}N^5H^{37} + 12HO.$$

The formula $C^{86}N^5H^{37}$ (vid. *Calculation* II) may be referred to the benzylene series in various ways: *e.g*, $C^{84}CyAd^3NH^{31}$; $C^{84}Ad^2N^2H^{32},CyH$; $C^{84}CyAd^2N^2H^{31},H^2$, &c. [L.].

Azobenzoide when heated yields an oil and a solid sublimate.

Insoluble in alcohol and ether.

## Azobenzoidin. $C^{86}N^5H^{37}$. ?

LAURENT. (1841.) *N. Ann. Chim. Phys.* 1, 302; *Ann. Pharm.* 38, 329; *Pharm. Centr.* 1841, 50.

*Formation and Preparation.* From crude bitter almond oil and ammonia (p. 25). Purified by two crystallisations from ether.

*Properties.* Colourless, microscopic, six-sided, oblique rhombic tables with dihedral summits. Inodorous. Melts when heated, and solidifies on cooling into a non-crystalline transparent mass.

| | Laurent. |
|---|---|
| C | 83·32 |
| N | 11·50 |
| H | 5·55 |
| | 100·37 |

Isomeric with azobenzoide (and azobenzoilide ?).

Nitric acid dissolves it with decomposition; and the solution on cooling deposits small needles which are nearly insoluble in water, but are dissolved by ammonia. — It dissolves with yellow colour in hot sulphuric acid, and ammonia added to the solution throws down a white substance. — It is decomposed by boiling with hydrochloric acid (with evolution of hydrocyanic acid? *comp.* Laurent & Gerhardt, *Compt. chim.* 1850, 113).

Nearly insoluble in alcohol, sparingly soluble in ether.

---

## Benzimide.

$C^{46}N^{2}H^{18}O^{4} = C^{42}Cy^{2}H^{18}O^{4}$.

LAURENT. (1836.) *Ann. Chim. Phys.* 59, 397; *Ann. Pharm.* 17, 88; *Pogg.* 36, 497.—*Ann. Chim. Phys.* 66, 193. — *Rev. scient.* 10, 120; *J. pr. Chem.* 27, 309; *Pharm. Centr.* 1836, 127; 1842, 242.
ZININ. *Ann. Pharm.* 34, 188; *Pharm. Centr.* 1840, 460.
GREGORY. *Ann. Pharm.* 54, 372.
LAURENT & GERHARDT. *Compt. chim.* 1850, 116; *Compt. rend.* 30, 404.

*Hydrure de cyanobenzoïle.*

*Formation.* By the action of hydrocyanic acid on bitter almond oil.

$$3C^{14}H^{6}O^{2} + 2C^{2}NH = C^{46}N^{2}H^{18}O^{4} + 2HO.$$

Occurs in crude bitter almond oil (Winckler, *Repert.* 92, 328).

*Preparation.* 1. Pure bitter almond oil mixed with one-fourth of its volume of nearly anhydrous prussic acid, is shaken up with an equal volume of concentrated alcoholic solution of potash diluted with 6 pts. of alcohol, then gently heated and left to stand for some time; and the white, curdy, flocculent precipitate which then falls down, is separated from the oil, boiled with water which extracts benzoïn, and purified by solution in alcohol. (Zinin.) Gregory obtained benzimide by leaving crude bitter almond oil in contact with potash-ley for ten years. According to Zinin, bitter almond oil containing a very large quantity of prussic acid, always yields benzimide instead of benzoïn when treated with potash-ley. — 2. When the resinous mass chiefly consisting of benzoïn and benzimide, which remains in the retort when bitter almond oil is rectified, is dissolved in boiling alcohol, a solution is obtained which on cooling yields benzimide, to be purified by several recrystallisations from hot alcohol. (Winckler.)

*Properties.* Colourless, light, somewhat pearly flakes composed of microscopic needles and laminæ. (Laurent.) White or greenish white, loosely coherent mass, which leaves a stain when rubbed or pressed. (Zinin.) Light, microscopic, yellowish white crystals, which are destitute of lustre and leave a stain. (Gregory.) Melts when heated and solidifies in a radiated mass at 167°. (Laurent.) Melts without decomposition at a high temperature. (Gregory.) Inodorous. May be volatilised without decomposition. (Laurent.)

| | | | | Laurent. | Zinin. | Gregory. |
|---|---|---|---|---|---|---|
| 46 C | 276 | 77·89 | | 76·46 | 77·28 | 77·67 |
| 2 N | 28 | 7·99 | | 7·00 | 7·76 | 8·20 |
| 18 H | 18 | 5·08 | | 4·94 | 5·09 | 5·17 |
| 4 O | 32 | 9·04 | | 11·6]0 | 9·87 | 8·96 |
| $C^{46}N^2H^{18}O^4$ | 354 | 100·00 | | 100·00 | 100·00 | 100·00 |

*Decompositions.* 1. When strongly heated, it turns brown, and volatilises, leaving charcoal. (Zinin.) Decomposes at a strong heat, and emits the odour of bitter almond oil. (Gregory.) Burns on platinum foil with a red sooty flame. (Laurent.)—2. Dissolves in hot *nitric acid* without evolution of nitrous vapours, and is not precipitated therefrom by water or ammonia. Heated with nitric acid and alcohol, it gives off red fumes and yields ammonia and benzoate of ethyl. (Laurent.) Dissolves in nitric acid with decomposition. (Zinin.)—3. Dissolves with decomposition in boiling *hydrochloric acid,* and yields an oil having the odour of bitter almond oil. (Laurent.) Boiled with hydrochloric acid, it yields bitter almond oil and sal-ammoniac (Gregory), probably also formic acid (Gerhardt, *Traité* 3, 194; compare *Compt. chim.* 1850, 116);

$$C^{46}N^2H^{18}O^4 + 10HO = 3C^{14}H^6O^2 + 2C^2H^2O^4 + 2NH^3.$$

4. When heated with *oil of vitriol,* it yields an emerald-green solution which afterwards turns yellow and then black, while benzoic acid sublimes. (Laurent.) When perfectly dry, it dissolves in fuming oil of vitriol with dark indigo colour; when somewhat moist, with emerald-green colour, which afterwards changes to yellow. (Laurent.) It dissolves in oil of vitriol with emerald-green colour which soon turns to red, and is precipitated in its original state by water. (Zinin, Gregory.) —5. Heated with strong bases it yields benzol. (Gregory.) Heated with hydrate of potash which is moistened with a little alcohol, it yields ammonia and benzoate of potash. (Laurent.)

*Combinations.* Insoluble in water. Dissolves sparingly in boiling *alcohol* and *ether* (Laurent, Zinin, Gregory), better in *wood-spirit.* (Laurent.)

## Thiobenzaldin.

$C^{42}NH^{19}S^{4} = C^{42}AdH^{17},S^{4}$ or $C^{42}AdH^{15}S^{2},2HS$.

LAURENT. (1841.) *N. Ann. Chim. Phys.* 1, 295; *Ann. Pharm.* 38, 323. — *Rev. scient.* 16, 393. — *Compt. rend.* 31, 352; *Pharm. Centr.* 1841, 498.

*Sulfobenzoylwasserstoff, Hydrure de sulfazobenzoïle, Sulfazoture de benzène.*

*Formation.* By the action of hydrosulphate of ammonia on bitter almond oil, the first stage of the reaction being probably the formation of sulphide of stilbene:

$$3C^{28}H^{12}S^{4} + 2NH^{3} = 2C^{42}NH^{19}S^{4} + 4HS.$$

*Preparation.* 1. Generally produced in small quantity in the preparation of sulphide of stilbene from bitter almond oil and hydrosulphate of ammonia; crystallises from the filtered alcoholic solution by spontaneous evaporation (p. 169). — 2. To a solution of 1 vol. crude bitter almond oil in 4 or 5 vol. ether, 1 vol. hydrosulphate of ammonia is added, and the crystalline crust which forms in the course of three or four weeks is purified by recrystallisation from ether. — 3. When 1 or 2 vol. hydrosulphate of ammonia are poured upon 1 vol. bitter almond oil, the greater part solidifies in 4 — 8 weeks, sometimes in a resinous, sometimes in a crystalline mass, which may be freed from adhering oily substance by washing with ether, and repeatedly crystallised from boiling ether. — In this reaction several compounds are formed (p. 25). By the third process, Laurent on one occasion obtained benzoylazotide and a thick oil; sometimes benzoylazotide or a white powder insoluble in ether is formed, in addition to thiobenzaldin. In one instance, rhombohedrons resembling calcspar and insoluble in ether were also produced.

*Properties.* Colourless laminæ with a pearly lustre, or when obtained by spontaneous evaporation of the ethereal solution, rather large oblique rectangular prisms belonging to the oblique prismatic system. *Fig.* 97, without *f* and *h* and with the *m*-faces predominating [oP. ∞P∞. (∞P∞.) ∞P] *i* : *t* nearly = 129°, in other crystals = 98°, *u* : *u* = 121° 40′; *y* : *u* = 122° 30′. Exhibits three distinct cleavages, the most distinct being parallel to *m*. Melts at 125°, becomes ductile on cooling and solidifies to a gummy mass. It imparts to the fingers an offensive odour, like sulphide of stilbene.

| | | | | Laurent. |
|---|---|---|---|---|
| 42 C | 252 | 72·21 | | 72·31 |
| N | 14 | 4·01 | | 3·20 |
| 19 H | 19 | 5·44 | | 5·31 |
| 4 S | 64 | 18·34 | | 18·00 |
| $C^{42}NH^{19}S^{4}$ | 349 | 100·00 | | 98·82 |

This compound occupies in the benzylene series the same place as thialdin in the ethylene series. Laurent, from the above analysis, deduced the formula $C^{126}N^{3}H^{56}S^{12}$, for which he afterwards (*Compt. rend.* 31, 352) substituted the one above given, in accordance with a new nitrogen-determination.

*Decompositions.* 1. Thiobenzaldin when strongly heated becomes bluish, then reddish and gives off ammonia; on cooling, the mass solidifies with a radiating structure. When distilled, it yields an oil and most of the products of decomposition of sulphide of stilbene. — 2. It is decomposed with effervescence by *bromine,* forming hydrobromate of ammonia, and an oil which may be extracted by ether and crystallises partially when its solution is evaporated. — 3. When moderately heated with *nitric acid,* it is violently attacked, an oil, which appears to be bitter almond oil, collecting on the surface. On boiling the liquid, benzoic acid is produced. — 4. With hot *oil of vitriol* it forms a solution of a beautiful carmine colour. Water destroys this colour and throws down yellow flakes. — 5. Boiled with alcoholic *potash,* it gives off ammonia; water added to the solution separates an oil which crystallises on exposure to the air, and acids eliminate sulphuretted hydrogen. — When continuously boiled with alcohol, it gives off sulphuretted hydrogen.

It dissolves in 20—30 pts. of boiling *ether.*

*Appendix to Thiobenzaldin:*

## Hydrosulphate of Azobenzoyl.

LAURENT. *N. Ann. Chim. Phys.* 1, 300; *Ann. Pharm.* 38, 327; *Pharm. Centr.* 1841, 500.

*Formation and Preparation.* A mixture of 1 vol. crude bitter almond oil, 1 vol. hydrosulphate of ammonia and 1 vol. ammonia, left to itself for a quarter of a year in a closed vessel, solidifies for the most part, and on treating the resulting mass with boiling ether, a small quantity of hydrosulphate of azobenzoyl remains behind.

White crystalline powder consisting of microscopic rhombs or rhomboïds, often having their acute edges truncated. Inodorous.

| | | | Laurent. |
|---|---|---|---|
| 42 C | 252 | 72·84 | 71·2 |
| 2 N | 28 | 8 09 | 8·7 |
| 18 H | 18 | 5·20 | 5·2 |
| 3 S | 48 | 13·87 | 12·0 |
| $C^{42}N^2H^{18}S^3$ | 346 | 100·00 | 97·1 |

As the analysis shows a loss of 3 per cent., Laurent placed but little confidence in the formula deduced from it.—The compound is perhaps $C^{42}N^2H^{21}S^3 = C^{42}Ad^2H^{16}S,2HS$, and produced in the manner represented by the equation :

$$3C^{28}H^{12}S^4 + 4NH^3 = 2C^{42}N^2H^{21}S^3 + 6HS \text{ [L.]}.$$

It is nearly insoluble in *alcohol* and dissolves but sparingly in boiling *ether.*

## Benzoylureide. $C^{50}N^{8}H^{28}O^{8}$.

LAURENT & GERHARDT. *Compt. chim.* 1850, 119; *Compt. rend.* 30, 405.

*Formation.* By the action of urea on bitter almond oil:

$$3C^{14}H^{6}O^{2} + 4C^{2}N^{2}H^{4}O^{2} = C^{50}N^{8}H^{28}O^{8} + 6HO.$$

*Preparation.* A mixture of 5 pts. of pulverised urea and 2 pts. bitter almond oil becomes perfectly liquid when heated to a temperature even below 100°, and soon afterwards solidifies into a compact mass. It is best to place the mixture in a basin on the sand-bath, and stir it with a pestle. The solid mass is pulverised, freed from any excess of bitter almond oil by treatment with ether, boiled with a large quantity of water till no more urea crystallises from the filtrate by evaporation, and dried at 120°.

*Properties.* Amorphous white powder destitute of taste and smell. Separates from the alcoholic solution by evaporation in amorphous crusts.

| | | | Laurent & Gerhardt. |
|---|---|---|---|
| 50 C | 300 | 59·52 | 59·70 |
| 8 N | 112 | 22·22 | 21·68 |
| 28 H | 28 | 5·55 | 5·54 |
| 8 O | 64 | 12·71 | 13·08 |
| $C^{50}N^{8}H^{28}O^{8}$ | 504 | 100·00 | 100·00 |

*Decompositions.* 1. Benzoylureide turns yellow at 170°, and gives off bitter almond oil at a temperature a few degrees higher. By dry distillation, it yields bitter almond oil and water containing ammonia, and leaves a yellow residue which dissolves sparingly in alcohol and ether, and disappears completely when more strongly heated. — 2. When boiled with dilute acids, it is resolved into bitter almond oil and urea. — 3. It is gradually decomposed by boiling potash-ley, bitter almond oil and ammonia escaping together with the watery vapours. The solution contains benzoate of potash.

Benzoylureide is insoluble in water.

It dissolves in *alcohol*, but not in ether.

## Benzoïnam.

$$C^{28}NH^{12}O = C^{28}AdH^{10}O?.$$

LAURENT. (1844.) *Compt. chim.* 1845, 37; *Pharm. Centr.* 1845, 829.

*Formation.* — By the action of alcoholic ammonia on benzoïn:

$$C^{28}H^{12}O^{4} + NH^{3} = C^{28}NH^{12}O + 3HO.$$

It is sometimes produced by the action of ammonia on crude bitter almond oil, probably because that substance almost always contains benzoïn.

*Preparation.* When the mixture obtained from benzoïn and alcoholic ammonia left to stand quietly (p. 174), is exhausted by boiling with alcohol, benzoïnam remains together with the crystalline body (2) (p. 174); on boiling this mixture with alcoholic potash, the body (2) dissolves, and the liquid is then somewhat diluted with alcohol and filtered. The filtrate mixed with water yields a precipitate, which however does not consist of the compound (2) in its original state. The benzoïnam remaining on the filter is dissolved in boiling alcohol containing a small quantity of hydrochloric acid, and precipitated from the solution by ammonia.

White microscopic needles. Inodorous. Melts when heated and crystallises partially in needles on cooling.

| | | | Laurent. |
|---|---|---|---|
| 28 C | 168 | 83·15 | 82·9 |
| N | 14 | 6·90 | 7·4 |
| 12 H | 12 | 5·90 | 5·9 |
| O | 8 | 4·05 | 3·8 |
| $C^{28}NH^{12}O$ | 202 | 100·00 | 100·0 |

The compound does not appear to be decomposed by potash.

It dissolves at a gentle heat in oil of vitriol, forming a reddish solution from which water throws down orange-yellow flakes.

It dissolves readily in boiling alcohol containing hydrochloric acid, and the solution, when diluted with water, deposits a portion of the benzoïnam, the rest on addition of ammonia.

## Benzoïnamide.

$C^{84}N^4H^{36} = C^{84}Ad^3N^3H^{33}$.?

LAURENT. (1837.) *Ann. Chim. Phys.* 66, 189; *Pharm. Centr.* 1838, 295.

*Formation.* By the action of aqueous ammonia on benzoïn:

$$3C^{28}H^{12}O^4 + 4NH^3 = C^{84}N^4H^{36} + 12HO.$$

*Preparation.* Benzoïn covered with ammonia in a stoppered bottle, forms in 8 weeks a white powder which may be freed from unaltered benzoin by boiling with alcohol. The residue is recrystallised from boiling ether.

*Properties.* White powder consisting of microscopic, very slender needles, having a silky lustre. After fusion, it solidifies in a fibrous mass. May be distilled without decomposition.

| | | | Laurent. |
|---|---|---|---|
| 84 C | 504 | 84·56 | 83·45 |
| 4 N | 56 | 9·40 | 8·94 |
| 36 H | 36 | 6·04 | 5·55 |
| $C^{84}N^4H^{36}$ | 596 | 100·00 | 97·94 |

Polymeric or isomeric with hydrobenzamide.

Insoluble in water; very sparingly soluble in *alcohol* and *ether*.

## Imabenzile.

$C^{28}NH^{11}O^{2} = C^{28}AdH^{9}O^{2}$ or $C^{28}NH^{11},O^{2}$.?

LAURENT. (1843.) *Rev. scient.* 10, 122; 19, 442; *J. pr. Chem.* 27, 312; 35, 463; *Pharm. Centr.* 1843, 243.

*Formation.* By the action of ammonia on benzile:

$$C^{28}H^{10}O^{4} + NH^{3} = C^{28}NH^{11}O^{2} + 2HO.$$

*Preparation.* Benzile is dissolved in warm absolute alcohol, dry ammoniacal gas passed through the still warm solution, and the liquid left to cool, while the passage of the gas is continued. After 24 hours, the liquid, together with the sediment which has formed, is heated to the boiling point, and filtered at the same temperature. Imabenzile then remains on the filter and may be purified by washing with ether.

*Properties.* White inodorous powder. Separates from its solution in boiling ether-alcohol, in microscopic right rhombic prisms with dihedral summits whose faces rest on the obtuse lateral edges. Melts at 140°, remains soft and glutinous on cooling, and then solidifies without crystallising.

| | | | | Laurent. |
|---|---|---|---|---|
| 28 C | 168 | 80·38 | 80·0 | 80·34 |
| N | 14 | 6·71 | 7·3 | 6·80 |
| 11 H | 11 | 5·26 | 5·3 | 5·18 |
| 2 O | 16 | 7·65 | 7·4 | 7·68 |
| $C^{28}NH^{11}O^{2}$ | 209 | 100·00 | 100·0 | 100·00 |

*Decompositions.* 1. Imabenzile is partially decomposed during fusion. When subjected to dry distillation, it neither gives off gas nor leaves any carbonaceous residue. — 2. When gently heated with nitric acid, it gives off red vapours, and yields a yellow oil, which solidifies in the crystalline form on cooling, dissolves in alcohol, and crystallises therefrom in small needles united in tufts, but is insoluble in ammonia. — 3. It is not altered by boiling with hydrochloric acid. It dissolves in gently heated oil of vitriol, and the solution mixed with water deposits benzilam. — 4. It dissolves readily in boiling alcoholic potash; and water added to the solution throws down benzilimide, while nothing but potash remains dissolved.

Imabenzile is perfectly insoluble in boiling alcohol and ether.

## Benzilim.

$C^{56}N^{2}H^{22}O^{4} = C^{56}Ad^{2}H^{18}O^{4}$.

LAURENT. (1845). *Rev. scient.* 19, 442; *J. pr. Chem.* 35, 463.

*Benzilimide.*

*Formation.* 1. By the action of ammonia on benzile:

$$2C^{28}H^{10}O^{4} + 2NH^{3} = C^{56}N^{2}H^{22}O^{4} + 4HO.$$

2. By boiling imabenzile with alcoholic potash.

*Preparation.* The hot filtrate obtained in the preparation of imabenzile (p. 218), deposits on cooling slender needles of benzilim, mixed with a few thick crystals of benzilam. The decanted mother-liquor yielded by spontaneous evaporation a few more crystals of benzilim together with crystals of benzilam. The benzilim is purified by several recrystallisations from boiling alcohol. 2. Imabenzile is dissolved in boiling alcoholic potash, and the solution mixed with water, which throws down benzilim.

*Properties.* White, silky, extremely slender needles, which, under the microscope, appear to be united in tufts. Melts at 130°, becomes gummy on cooling, and solidifies at ordinary temperatures, without crystallising.

| | | | Laurent. |
|---|---|---|---|
| 56 C | 336 | 80·38 | 80·0 |
| 2 N | 28 | 6·71 | 7·0 |
| 22 H | 22 | 6·26 | 5·6 |
| 4 O | 32 | 7·65 | 7·4 |
| $C^{56}N^{2}H^{22}O^{4}$ | 418 | 100·00 | 100·0 |

Polymeric (or isomeric) with imabenzile.—Laurent (*Méthode de chimie*, p. 108) regards it as the nitrile of benzilic acid = $C^{28}NH^{11}O^{2}$.

*Decompositions.* 1. When fused, it yields the same products of decomposition as imabenzile. Distils apparently without decomposition, but the distillate dissolves very readily in ether and crystallises therefrom in needles by evaporation. — 2. It is easily decomposed by hot nitric acid, with evolution of red vapours, and yields the same products as imabenzile. — 3. It dissolves in gently heated oil of vitriol, and the solution mixed with water deposits benzilam. — 4. It is not decomposed by hydrochloric acid.

It dissolves sparingly in *alcohol* and *ether*.

## Benzilam. $C^{28}NH^{9}$.

LAURENT. (1845.) *Rev. scient.* 19, 443; *J. pr. Chem.* 35, 464.

*Formation.* 1. By the action of ammonia on benzile:

$$C^{28}H^{10}O^{4} + NH^{3} = C^{28}NH^{9} + 4HO.$$

2. By dissolving imabenzile or benzilim in oil of vitriol:

$$C^{28}NH^{11}O^{2} = C^{28}NH^{9} + 2HO.$$

*Preparation.* 1. The thick crystals obtained in the preparation of benzilim are purified by repeated crystallisation from cold ether-alcohol. — 2. The solid mass obtained by the action of ammonia on benzile is washed with alcohol; the resulting mixture of imabenzile and benzilim

dissolved in gently heated oil of vitriol; and the solution diluted with water; an oil then separates out which solidifies almost immediately. This product is washed with water, then quickly with a small quantity of alcohol, dissolved in ether-alcohol, and the solution is left to evaporate.

*Properties.* Colourless, right rectangular prisms. *Fig.* 69 without *p* and *i*, and very narrow ($\infty \breve{P}\infty$ . $\infty \bar{P}\infty$ . $\bar{P}\infty$). $y : y' = 106°$; $t : m = 90°$; $t : u = 115°$. Crystallises from alcohol in prisms an inch or two long; from ether in short, rather thick prisms.—Melts at 105°, and if not perfectly fused, solidifies again in needles at a temperature very little lower; but after complete fusion, it remains fluid for a long time at ordinary temperatures, and gradually solidifies without crystallising, but if it be then gently warmed, becomes opaque and crystalline.

| | | | | Laurent. |
|---|---|---|---|---|
| 28 C | 168 | .... | 87·94 | ..... 87·63 |
| N | 14 | .... | 7·33 | ..... 7·00 |
| 9 H | 9 | .... | 4·73 | ..... 5·00 |
| $C^{28}NH^{9}$ | 191 | .... | 100·00 | ..... 99·63 |

It is quickly decomposed by nitric acid, an oil being produced which crystallises in needles on cooling and is insoluble in ether.

It is not decomposed by boiling alcoholic potash.

It dissolves readily in *oil of vitriol*, and is precipitated in its original state by water.

It dissolves very easily in *alcohol* and in *ether*.

## Azobenzile. $C^{42}NH^{15}O^{2}$.

ZININ. (1840.) *Ann. Pharm.* 34, 190.
LAURENT *Rev. scient.* 19, 445; *J. pr. Chem.* 35, 466.

*Formation and Preparation.* When an alcoholic solution of benzile not too concentrated is mixed with aqueous ammonia, a white granular precipitate is formed, which, after remaining in the liquid for 10 hours, is washed and recrystallised from alcohol. The liquid which has deposited the azobenzile, contains benzoate of ethyl; and apparently, a body which dissolves readily in alcohol and crystallises in small needles [probably benzilam. L.]. The same substance is more abundantly produced when an alcoholic solution of benzile is gradually mixed with ammonia at the boiling heat, till the liquid, still kept boiling, exhibits a milky turbidity.

*Properties.* White, highly lustrous, iridescent, thin, smooth needles and laminæ.

| I. | | | | II. | | | | | Laurent. |
|---|---|---|---|---|---|---|---|---|---|
| 42 C | 252 | .... | 87·20 | 42 C | 252 | .... | 84·85 | .... | 84·39 |
| N | 14 | .... | 4·84 | N | 14 | .... | 4·71 | .... | 4·64 |
| 15 H | 15 | .... | 5·19 | 15 H | 15 | .... | 5·05 | .... | 5·18 |
| O | 8 | .... | 2·77 | 2 O | 16 | .... | 5·39 | .... | 5·79 |
| $C^{42}NH^{15}O$ | 289 | .... | 100·00 | $C^{42}NH^{15}O^{2}$ | 297 | .... | 100·00 | .... | 100·00 |

Laurent, adopting Zinin's formula (I) gives for the formation of azobenzile the equation:

$$5C^{28}H^{10}O^4 + 2NH^3 = 2C^{42}NH^{15}O + 4C^{14}H^6O^4 + 2HO,$$

which likewise takes account of the simultaneous formation of benzoate of ethyl. According to formula (II), the formation of azobenzile takes place simultaneously with that of benzoic acid and benzilam, as represented by the equation:

$$4C^{28}H^{10}O^4 + 3NH^3 = C^{42}NH^{15}O^2 + 2C^{28}NH^{19} + C^{14}H^6O^2 + 10HO \text{ [L.]}.$$

Azobenzile is nearly insoluble in water, potash and ammonia.

It dissolves in alcoholic potash, ammonia, and hydrochloric acid, whence it crystallises without alteration. The solution is not precipitated by alcoholic nitrate of silver.

Soluble in alcohol.

---

¶ *Addenda to the Benzylene Series.*

## Methylate of Benzylene.

$C^{18}H^{12}O^4 = C^{14}H^6(C^2H^3)^2O^4$.

C. Wicke. *Ann. Pharm.* 102, 363.

*Methylobenzolic ether, Methylbenzoläther.*

*Formation.* By the action of methylate of sodium on chloride of benzylene:

$$C^{14}H^6,Cl^2 + 2C^2H^3NaO^2 = 2NaCl + C^{14}H^6(C^2H^3)^2O^4.$$

*Preparation.* 2 At. sodium are dissolved in pure anhydrous methylic alcohol, and the solution boiled for some hours with chloride of benzylene. A large quantity of chloride of sodium then separates; the excess of methylic alcohol is removed by distillation at the heat of the water-bath; the residue mixed with water; and the methylate of benzylene, which rises to the surface, is removed by a pipette, then dried and rectified.

*Properties.* Transparent, colourless liquid, heavier than water. Boils at 208°, leaving however a brown residue arising from decomposition. — Has an agreeable odour, resembling that of geraniums. — Insoluble in water; easibly soluble in wood-spirit, alcohol, and ether.

## Ethylate of Benzylene.

$C^{22}H^{16}O^4 = C^{14}H^6(C^4H^5)^2O^4$.

Wicke. *Ann. Pharm.* 102, 364.

*Ethylobenzolic ether, Aethylbenzoläther.*

Prepared, like the preceding compound, by the action of ethylate of sodium on chloride of benzylene.

Transparent colourless liquid, heavier than water, and smelling like the methyl-compound. Boils at 222°.

| | | | Wicke. |
|---|---|---|---|
| 22 C | 132 | 73·33 | 73·01 |
| 16 H | 16 | 8·88 | 9·01 |
| 4 O | 32 | 17·79 | 17·98 |
| $C^{22}H^{16}O^4$ | 180 | 100·00 | 100·00 |

This and the preceding compound may be regarded as compound ethers derived from the [unknown] biatomic alcohol $\left.\begin{matrix}C^{14}H^6\\H^2\end{matrix}\right\}O^4$, related to chloride of benzylene $C^{14}H^6,Cl^2$, in the same manner as Wurtz's glycol or hydrate of ethylene $\left.\begin{matrix}C^4H^4\\H^2\end{matrix}\right\}O^4$, is related to chloride of ethylene, these alcohols being formed from 2 molecules of water, $\left.\begin{matrix}H^2\\H^2\end{matrix}\right\}O^4$ by the replacement of 2 At. H by the biatomic radicals $C^{14}H^6$ and $C^4H^4$. The ethers are formed by the replacement of the other two atoms of hydrogen by 2 At. methyl, or ethyl, &c.; thus *ethylate of benzylene* $= \left.\begin{matrix}C^{14}H^6\\(C^4H^5)^2\end{matrix}\right\}O^4$. This compound occupies in the benzylene series the same place that acetal $\left.\begin{matrix}C^4H^4\\(C^4H^5)^2\end{matrix}\right\}O^4$ occupies in the ethylene series.

Ethylate of benzylene is insoluble in water, but dissolves readily in *wood-spirit, alcohol* and *ether*.

## Amylate of Benzylene.

$$C^{34}H^{28}O^4 = C^{14}H^6.(C^{10}H^{11})^2O^4.$$

WICKE. *Ann. Pharm.* 102, 364.

*Amylobenzolic ether, Amylbenzoläther.*

Produced by the action of amylate of sodium on chloride of benzylene. It must be freed from adhering fusel-oil by fractional distillation, that liquid not being sufficiently soluble in water to be removable by washing.

Slightly yellowish oil, lighter than water, and having an odour somewhat like that of fusel oil. Boils, with some decomposition, at about 292°.

| | | | Wicke. |
|---|---|---|---|
| 34 C | 204 | 77·27 | 76·90 |
| 28 H | 28 | 10·60 | 10·37 |
| 4 O | 32 | 12·13 | 12·73 |
| $C^{34}H^{28}O^4$ | 264 | 100·00 | 100·00 |

## Acetate of Benzylene.

$C^{22}H^{12}O^8 = C^{14}H^6(C^4H^3O^2)^2O^4$.

WICKE. *Ann. Pharm.* 102, 366.

*Acetobenzolic ether, Essigsäure-Benzoläther.*

*Formation.* By the action of chloride of benzylene on acetate of silver:

$$C^{14}H^6,Cl^2 + 2\left(\left.\begin{matrix}C^4H^3O^2\\Ag\end{matrix}\right\}O^2\right) = 2AgCl + \left.\begin{matrix}C^{14}H^6\\(C^4H^3O^2)^2\end{matrix}\right\}O^4.$$

*Preparation.* Perfectly dry acetate of silver (rather more than 2 At.) is triturated with 1 At. chloride of benzylene, and the scarcely moist mixture introduced into a small flask. On the application of a gentle heat, a violent action takes place, attended with evolution of white fumes; hence it is best not to use more than 10 grammes of the silver-salt at a time; but even then the product falls considerably below the calculated quantity. The mass, after cooling, is treated with successive portions of ether as long as that liquid dissolves any thing out of it; the united ethereal extracts distilled in the water-bath; the residual yellowish oil freed from adhering acetic acid by washing with weak soda-ley and then with water, and finally redissolved in a small quantity of ether; and the solution is left to evaporate. The acetate of benzylene then remains in the form of a viscid oil, which deposits small macle-crystals in the course of 24 hours, and after some time solidifies completely.

*Properties.* Small, perfectly white, shining crystals, very much resembling the so-called swallow-tail crystals of gypsum and apparently belonging to the oblique prismatic system. From solution in alcohol or ether it separates by spontaneous evaporation, as an oil, and is likewise precipitated as an oil on adding water to the alcoholic solution. This oil often remains liquid for a considerable time, but suddenly solidifies on being touched with an angular body or on agitation. — The compound melts at 136° and solidifies in the crystalline form on cooling.

| | | | Wicke. |
|---|---|---|---|
| 22 C | 132 | 63·5 | 63·6 |
| 12 H | 12 | 5·8 | 6·1 |
| 8 O | 64 | 30·7 | 30·3 |
| $C^{22}H^{12}O^8$ | 208 | 100·0 | 100·0 |

*Decompositions.* 1. Acetate of benzylene cannot be volatilised without decomposition. When heated in a retort, it begins to boil at 190°, the boiling point gradually rising to 240°. The distillate, which is acid to moist litmus paper, is a mixture of anhydrous acetic acid and bitter almond oil:

$$\left.\begin{matrix}C^{14}H^6\\(C^4H^3O^2)^2\end{matrix}\right\}O^4 = (C^4H^3O^2)^2,O^2 + C^{14}H^6O^2.$$

2. Heated with aqueous potash to 100° in a sealed tube, it yields bitter almond oil and acetate of potash:

$$\left.\begin{matrix}C^{14}H^{6}\\(C^{4}H^{3}O^{2})^{2}\end{matrix}\right\}O^{4} + 2HO = C^{14}H^{6}O^{2} + 2C^{4}H^{4}O^{4}.$$

This reaction is not exactly analogous to that of acetate of ethylene $\left.\begin{matrix}C^{4}H^{4}\\(C^{4}H^{3}O^{2})^{2}\end{matrix}\right\}O^{4}$ with aqueous potash, which yields glycol or hydrate or ethylene $\left.\begin{matrix}C^{4}H^{4}\\H^{2}\end{matrix}\right\}O^{4}$. A similar decomposition of acetate of benzylene would yield benzolic alcohol or hydrate of benzylene $\left.\begin{matrix}C^{14}H^{6}\\H^{2}\end{matrix}\right\}O^{4}$.—3. Acetate of benzylene heated to 100° in a sealed tube with aqueous ammonia, yields acetamide and hydrobenzamide, the former of which may be extracted from the mixture by solution in water.

$$3\left(\left.\begin{matrix}C^{14}H^{6}\\(C^{4}H^{3}O^{2})^{2}\end{matrix}\right\}O^{4}\right) + 8NH^{3} = 6N(H.H.C^{4}H^{3}O^{2}) + C^{42}N^{2}H^{18} + 12HO.$$

4. Heated to 100° in a sealed tube with dilute sulphuric acid, it is converted into bitter almond oil.

*Combinations.* Insoluble in water, but dissolves very readily in *alcohol* and *ether*.

## Valerate of Benzylene.

$$C^{34}H^{24}O^{8} = C^{14}H^{6}(C^{10}H^{9}O^{2})^{2}O^{4}.$$

WICKE. *Ann. Pharm.* 102, 369.

*Valerobenzolic ether, Valeriansäure-Benzoläther.*

Prepared like the acetate, by the action of chloride of benzylene on valerate of silver. After the action is completed, the mass is not solid but viscid, and ether extracts from it an oil, which, when the solvent is evaporated, remains viscid and yellow, and cannot be induced to crystallise.

| | | | Wicke. |
|---|---|---|---|
| 34 C | 204 | 69·8 | 67·9 |
| 24 H | 24 | 8·2 | 7·6 |
| 8 O | 64 | 22·0 | 24·5 |
| $C^{34}H^{24}O^{8}$ | 292 | 100·0 | 100·0 |

The difference between the analytical and calculated results arises from the presence of excess of chloride of benzylene, which could not be removed.

The compound is decomposed by distillation, apparently in the same manner as the acetate; for the distillate treated with carbonate of soda, slowly gives up valerianic acid, while bitter almond oil remains behind:

$$\left.\begin{matrix}C^{14}H^{6}\\(C^{10}H^{9}O^{2})^{2}\end{matrix}\right\}O^{4} = C^{14}H^{6}O^{2} + (C^{10}H^{9}O^{2})^{2},O^{3}.$$

## Benzoate of Benzylene.

$C^{42}H^{16}O^{8} = C^{14}H^{6}(C^{14}H^{5}O^{2})^{2}O^{4}$.

WICKE. *Ann. Pharm.* 102, 370.

When chloride of benzylene is triturated with benzoate of silver, the mixture becomes heated, acquires a kneadable consistence, and must be quickly introduced into a flask provided with an escape-tube to carry away the intensely suffocating vapours of chloride of benzylene. On treating the cooled mass with ether, a brown extract is obtained, which when evaporated, yields a viscid, brown, uncrystallisable mass. This product mixed with alcoholic potash immediately yields a solid mass of benzoate of potash, together with bitter almond oil.

---

Benzylene likewise unites with bibasic acids, forming compounds which may be regarded as benzolic alcohol in which the 2 At. of basic hydrogen are replaced by the radical of a bibasic acid.

*Sulphate of Benzylene.* — $\left.\begin{matrix}C^{14}H^{6}\\S^{2}O^{4}\end{matrix}\right\}O^{4}$, obtained by the action of chloride of benzylene on sulphate of silver, is a red-brown, uncrystallisable oil.

*Succinate of Benzylene.* — $\left.\begin{matrix}C^{14}H^{6}\\C^{8}H^{4}O^{4}\end{matrix}\right\}O^{4}$, appears to be formed by the action of chloride of benzylene on succinate of silver. The ethereal extract treated with dilute soda-ley, yields free succinic acid and bitter almond oil.

The action of chloride of benzylene on oxalate of silver is so violent that no definite product can be obtained from it.

---

Chloride of benzylene heated to 100° in a sealed tube with strong aqueous or alcoholic potash (most quickly by the latter) yields chloride of potassium and bitter almond oil.

$$C^{14}H^{6},Cl^{2} + 2KO = C^{14}H^{6}O^{2} + 2KCl.$$

The statement of Cahours (p. 51) that this compound is not acted upon by potash, is therefore incorrect.

Heated for some time to 100° with aqueous or alcoholic ammonia in a sealed tube, it yields sal-ammoniac and bitter almond oil. At ordinary temperatures no action takes place. Chloride of benzylene may also be distilled without change in dry ammoniacal gas.

Heated to 100° in a sealed tube with an alcoholic solution of sulphocyanide of potassium, it yields chloride of potassium and an oil having the odour of mustard-oil. With dry cyanide of potassium at 100°, no decomposition takes place. (Wicke.) ¶.

*Toluene Series.*

A. PRIMARY SERIES.

*Primary Nucleus* $C^{14}H^{8}$.

## Toluene or Toluol. $C^{14}H^{8}$.

PELLETIER & WALTER. (1837.) *Ann. Chim. Phys.* 67, 269; *Pogg.* 44, 81; *Pharm. Centr.* 1837, 551.
COUERBE. *Ann. Chim. Phys.* 69, 184; *J. pr. Chem.* 18, 65.
DEVILLE. *N. Ann. Chim. Phys.* 3, 152, 168; *J. pr. Chem.* 25, 336; abstr. *J. Pharm.* 27, 636, 640; *Pharm. Centr.* 1842, 194.
GLÉNARD & BOUDAULT. *N. Ann. Chim. Phys.* 4, 274; abstr. *Compt. rend.* 17, 503; also *J. pr. Chem.* 31, 111. — *N. J. Pharm.* 6, 250; abstr. *Compt. rend.* 19, 505; *J. pr. Chem.* 33, 466; *Pharm. Centr.* 1844, 155.
BLYTH & HOFMANN. *Ann. Pharm.* 53, 325.
MUSPRATT & HOFMANN. *Ann. Pharm.* 54, 9; *Pharm. Centr.* 1845, 514.
NOAD. *Ann. Pharm.* 63, 305.
E. KOPP. *Compt. chim.* 1849, 149.
MANSFIELD. *Chem. Soc. Qu. J.* 1, 266; also *Ann. Pharm.* 69, 478.
CAHOURS. *Compt. rend.* 28, 384; also *J. pr. Chem.* 47, 423; *Compt. rend.* 30, 319.
WILSON. *Ann. Pharm.* 77, 216; *Chem. Soc. Q. J.* 3, 154.
VÖLCKEL. *Ann. Pharm.* 86, 334.
CANNIZZARO. *Ann. Pharm.* 90, 252; 96, 246.
RITTHAUSSEN. *J. pr. Chem.* 61, 74; *Pharm. Centr.* 1854, 350.

*Retinaphta* (Pelletier & Walter), *Heptacarbure quadrihydrique* (Couerbe), *Benzoen* (Deville), *Dracyl* (Glénard & Boudault), *Toluène* (Cahours). [*Tole*, Gm.].

*Formation.* 1. By the action of potash on benzylic alcohol. (Cannizzaro):

$$3C^{14}H^{8}O^{2} + KO,HO = C^{14}H^{5}KO^{4} + 2C^{14}H^{8} + 4HO.$$

2. By heating toluylic acid with excess of lime. (Noad):

$$C^{16}H^{8}O^{4} = C^{14}H^{8} + 2CO^{2}.$$

3. By the dry distillation of tolu balsam (Deville, Muspratt & Hofmann, E. Kopp); of dragon's blood (Glénard & Boudault); of the resin of *Pinus maritima* (Pelletier & Walter); of Burmese naphtha or Rangoon tar (De la Rue & Müller, *Proc. Roy. Soc.* 8, 221). — 4. In the preparation of illuminating gas from resin or of rather fat oil. (Couerbe.) — 5. In the dry distillation of wood (Völckel) and of coal. It occurs abundantly in coal-tar oil. (Mansfield.)

*Preparation.* 1. *From Benzylic alcohol.* — When benzylic alcohol is distilled with four or five times its volume of concentrated alcoholic potash in an apparatus which allows the less volatile products to flow back again, all the alcohol passes over at first, then water with a small quantity of unaltered benzylic alcohol, and at last, when the residue has

become solid, a mixture of toluol with benzylic alcohol. This mixture is distilled by itself; the portion which goes over at 116° collected apart and shaken up with oil of vitriol, whereby the benzylic alcohol is resinized and dissolved; and the decanted liquid is washed with carbonate of potash and twice rectified over anhydrous phosphoric acid. (Cannizzaro.)

2. *From Tolu balsam.* — The balsam freed by distillation with water from toluene, cinnamein and a portion of the benzoic acid, is heated in a copper boiler to remove the water, till it no longer froths up, and then subjected to dry distillation in a retort filled only to one-fourth. At first it boils quietly and gives off nearly pure benzoic acid (benzoic acid with a little cinnamic acid, which solidify in the receiver in the crystalline form, and yield a considerable quantity of toluol when distilled with water: Muspratt & Hofmann). The heat must then be increased to maintain the ebullition, which becomes irregular, the mass frothing up strongly and therefore requiring frequent agitation; at a later stage of the process, however, it again boils quietly. The product of the distillation is — besides carbonic acid, carbonic oxide and a little water — a heavy oil, which is a mixture of benzoate of ethyl (more probably benzoate of methyl according to Muspratt & Hofmann, also according to Scharling, *Ann. Pharm.* 97, 83), and toluol. This mixture is distilled by itself, and the portion which goes over between 130° and 140° is rectified over strong potash-ley and dried over chloride of calcium; the product is very small. (Deville, Muspratt & Hofmann.) — E. Kopp purifies tolu-balsam as completely as possible from cinnamic acid by repeated boiling with carbonate of soda, boils the residue with strong soda-ley, and distils the brown solution (which solidifies in a brown mass on cooling) at a gradually increasing heat. The oil which passes over with the water increases in quantity till it amounts to a tenth part of the distillate after decantation; it is rectified, dehydrated over chloride of calcium, and again rectified.

3. *From Dragon's blood.* — When the black-red oil obtained by the dry distillation of dragon's blood is rectified, a mixture passes over consisting of toluol and styrol (draconyl: *Glénard & Boudault*) which becomes colourless after being twice distilled with water; and when this mixture is repeatedly distilled at the lowest possible temperature, and without ebullition, in order to convert the styrol into metastyrol (or, to retain the draconyl, according to Glénard & Boudault), the toluol distils over. According to Glénard & Boudault, the toluol should ultimately be boiled several times with solid hydrate of potash to retain the draconyl; according to Blythe & Hofmann, the styrol is merely converted by the heat into metastyrol, and complete separation might be effected by heating the mixture for an hour to 200°.

4. In the distillation of *resin-oil* (x, 411), toluol passes over after the oil $C^{12}H^{8}$ (xi, 378). (Couerbe.) — 5. When the brown oil obtained in the preparation of illuminating gas by the dry distillation of the resin of *Pinus maritima* (*brai sec.*), is subjected to fractional distillation, there passes over between 130° and 160°, a yellowish red oil which has a strong but not unpleasant odour, reddens litmus, and when rectified leaves a carbonaceous residue, while an amber-coloured distillate passes over. This distillate is freed from the empyreumatic acid by agitation with tolerably strong potash-ley, and distilled in the oil-bath; the portion which distils over at 160° is shaken up with oil of vitriol; and the decanted oil is washed with potash-ley and rectified. This treatment with oil of vitriol and potash-ley is repeated 15 or 20 times, till the residual oil,

when again treated with oil of vitriol, neither becomes coloured itself, nor imparts any colour to the oil of vitriol, after which, it is rectified two or three times over potassium, till that metal remains in contact with it perfectly bright. (Pelletier & Walter.)

6. When crude commercial *wood-spirit* is diluted with water, a pale yellow oil whose boiling point varies from 90° to 260° rises to the surface. This oil is shaken up with oil of vitriol; and the clear liquid is decanted from the brown-red viscid mass, washed with dilute potash-ley, dried by chloride of calcium, and distilled over anhydrous phosphoric acid. The portion which first distils over (between 108° and 112°) is toluol. (Cahours.) —7. The portion of the volatile oil obtained in the distillation of *beech-tar*, which passes over between 100° and 150°, is treated with oil of vitriol, and the undissolved portion is subjected to fractional distillation. The portion which distils between 110° and 130° is toluol. (Völckel.) —8. The portion *c* (xi, 135) of the light naphtha obtained from coal-tar, which distils over between 100° and 150°, consists of toluol. (Mansfield, Ritthausen.) — The portion which goes over between 100° and 120° is treated with half its weight of oil of vitriol, whereby unknown substances are removed and a constant product more readily obtained (Wilson); see also Hilkenkamp, *Ann. Pharm.* 95, 86; *Chem. Gaz.* 1855, 461).

*Properties.* Colourless, strongly refracting oil, having a pleasant ethereal odour very much like that of benzol, and a burning taste. Sp. gr. 0·86 (Pelletier & Walter), 0·821 (Couerbe), 0·87 at 18° (Deville), 0·864 at 23° (Glénard & Boudault). Very mobile; does not solidify at −20°. (Pelletier & Walter; Glénard & Boudault). Boils at 108° when the barometer stands at 0·76 met. (Pelletier & Walter, Deville); at 100° (Couerbe), at 106° (Glénard & Boudault), at 114° (Gerhardt, *N. Ann. Chim. Phys.* 14, 107; *J. pr. Chem.* 35, 300; Cannizzaro), at 109°, bar. at 0·763 met., the boiling point rising gradually to 110·5° (Noad), from 110° to 110·5° (Ritthausen, Wilson), at 103·7° (Church, *Phil. Mag.* [4], 9, 256). Volatilises without decomposition. It becomes partially oxidised during distillation, if the vapours in the upper part of the retort become hotter than the boiling liquid. (Church.) — Vapour density = 3·23 (Pelletier & Walter) 3·34 (Couerbe), 3·26 (Deville), 3·27 (Cahours.)

| | | Pelletier & Walter. | Couerbe. | Deville. | Glénard & Boudault. | Noad. | Völckel. | Cannizzaro. |
|---|---|---|---|---|---|---|---|---|
| 14 C | 84 | 91·30 | 90·47 | 91·11 | 91·10 | 91·26 | 91·50 | 90·97 | 91·22 |
| 8 H | 8 | 8·70 | 8·90 | 8·67 | 9·06 | 8·78 | 9·03 | 9·02 | 8·77 |
| $C^{14}H^{8}$ | 92 | 100·00 | 99·37 | 99·78 | 100·16 | 100·04 | 100·53 | 99·99 | 99·99 |

| | Vol. | Density. |
|---|---|---|
| C-vapour | 14 | 5·8240 |
| H-gas | 8 | 0·5544 |
| Vapour of Toluol | 2 | 6·3784 |
| | 1 | 3·1892 |

*Decompositions.* 1. Vapour of toluol is not altered by passing through a red-hot tube filled with potash-lime. (Deville,) — 2. Toluol remains unaltered when left in contact with potash in vessels containing

air, or with platinum-black in vessels containing oxygen. (Deville.) It burns with a sooty flame. — 3. Toluol absorbs *chlorine gas*, with evolution of heat. (Glénard & Boudault.) When chlorine gas is passed in the dark through toluol kept at a low temperature, the action does not terminate in four hours. (The liquid, after being freed from excess of chlorine by passing a stream of carbonic acid gas through it at a temperature between 50° and 60°, contains only 13·87 per cent. of chlorine.) After the action of the chlorine has been continued for a week, the liquid contains 14 At. C, 7H and 2·5 Cl; on distilling it, chlorotoluol, $C^{14}ClH^{7}$, passes over first, without evolution of hydrochloric acid, but afterwards that acid is given off. When chlorine is passed into toluol in broad daylight, as long as hydrochloric acid continues to form, hydrochlorate of terchlorotoluol $C^{14}Cl^{3}H^{5},HCl$ is produced; after a still longer passage of the gas, liquid bihydrochlorate of terchlorotoluol $C^{14}Cl^{3}H^{5},2HCl$ is formed, together with crystals of terhydrochlorate of terchlorotoluol $C^{14}Cl^{3}H^{5},3HCl$. (Deville.) — At ordinary temperatures, toluol absorbs chlorine gas without being decomposed, but when chlorine is passed into toluol heated to the boiling point, the toluol is converted into an oil resembling chloride of benzoyl, which appears to be $C^{14}Cl^{2}H^{6}$, but cannot be completely purified by water from chlorine and hydrochloric acid. (Pelletier & Walter.) — 4. Fuming *nitric acid* converts toluol at ordinary temperatures into nitrotoluol $C^{14}XH^{7}$, and at the boiling heat, into binitrotoluol $C^{14}X^{2}H^{6}$. Dilute nitric acid acts slowly upon it, but ultimately yields the same products as the fuming acid. (Deville.) — Cold nitric acid does not act sensibly on toluol; but on distilling the liquid, nitrous vapours are given off, together with a large quantity of hydrocyanic acid; and in the retort there remains a warty mass, which when repeatedly boiled with alcohol, forms a white granular powder, which reddens litmus, dissolves in alkalis, is precipitated therefrom by acids, and sublimes when heated, leaving a carbonaceous residue. (Pelletier & Walter.) According to Glénard & Boudault, toluol (dracyl) forms with fuming nitric acid, when it acts in small quantity only, nitrotoluol (nitrodracyl), but in larger quantity and at a higher temperature, nitrodracylic acid $C^{16}XH^{6}O^{4}$[?], the action being attended with evolution of carbonic acid and red fumes. — 5. Toluol is scarcely attacked by boiling oil of vitriol (Pelletier & Walter); it dissolves in fuming sulphuric acid, with rise of temperature and formation of sulphotoluic acid and sulfitoluol. (Deville.) — Potassium and potash do not act upon toluol. (Pelletier & Walter, Glénard & Boudault.) Toluol digested with sodium in a closed vessel for 14 days, yields two substances boiling respectively at 97° and 112°. (Church, *Phil. Mag.* [4], 9, 256.)

*Combinations.* Toluol is insoluble in water, but imparts its odour to that liquid. (Deville, Glénard & Boudault.)

It dissolves *iodine* at ordinary temperatures with amber-red colour, and at higher temperatures a large quantity of *sulphur*, which separates in fern-like crystals on cooling. (Pelletier & Walter.)

It dissolves sparingly in alcohol, more readily in *ether* (Deville, Glénard & Boudault); it is soluble in *oils* both *fixed* and *volatile*, and dissolves most *resins*. (Pelletier & Walter, Glénard & Boudault.)

## Hydrate of Cresyl. $C^{14}H^{8}O^{2}$.

WILLIAMSON & FAIRLIE. *Chem. Soc. Qu. J.* 7, 232; *Chem. Gaz.* 1854, 376; *J. pr. Chem.* 63, 294.

*Cresylic alcohol.*

Occurs in variable quantity in creosote from coal-tar, and is obtained from the portion boiling between 200° and 220°, by fractional distillation, as a colourless, strongly refracting liquid, which boils at 203° in the air and at 200° in an atmosphere of hydrogen.

| | | | | | Fairlie. | | |
|---|---|---|---|---|---|---|---|
| 14 C | 84 | .... | 77·77 | ..... | 77·40 | .... | 77·69 |
| 8 H | 8 | .... | 7·41 | ..... | 8·05 | .... | 7·20 |
| 2 O | 16 | .... | 14·82 | ..... | 14·55 | .... | 15·11 |
| $C^{14}H^{8}O^{2}$ | 108 | .... | 100·00 | ..... | 100·00 | .... | 100·00 |

Isomeric or metameric with taurylic acid (xi, 154), and benzylic alcohol (xii, 18).

The compound is decomposed by repeated distillation in the ordinary way, a portion appearing to be converted by the oxidising action of the air into hydrate of phenyl; but in an atmosphere of hydrogen, it may be distilled any number of times without alteration. — *Nitric acid* at ordinary temperatures attacks it with explosive violence; but when treated with well cooled nitric acid, it yields a red solution containing *ternitrocresylic acid* $C^{14}X^{3}H^{5}O^{2}$ (xi, 228). Dilute nitric acid forms only a brown tarry mass. — With *oil of vitriol* it becomes rose-coloured, and forms *sulphocresylic acid* $C^{14}H^{8}O^{2},2SO^{3}$. The baryta-salt of this acid yielded by analysis 29·47 p. c. baryta, while the formula $C^{14}H^{7}BaO^{2},2SO^{3}$ requires 29·97 p. c. — With *pentachloride of phosphorus* it yields chloride of cresyl (which boiled at 197°) and phosphate of cresyl, which latter is converted by double decomposition with acetate of potash into acetate of cresyl. [Compare the action of $PCl^{5}$ on hydrate of phenyl (xi, 149, 173.)] Mixed with an equal bulk of strong potash-ley, it forms in the course of 24 hours, a few small crystals, apparently consisting of cresylate of potassium $C^{14}H^{7}KO^{2}$.

## Sulphotoluic Acid.

$C^{14}H^{8}S^{2}O^{6} = C^{14}H^{8},2SO^{3}$.

DEVILLE. (1841.) *N. Ann. Chim. Phys.* 3, 172.
GLÉNARD & BOUDAULT. *N. J. Pharm.* 6, 253.

*Toluolschwefelsäure, Acide sulfotoluènique, Acide sulfobenzoènique, Acide sulfodracylique.*

*Formation.* From toluol and fuming oil of vitriol (p. 229).

*Preparation.* Fuming oil of vitriol is saturated with toluol; the mass which solidifies on cooling is treated with water; the solution filtered from the sulfitoluol, is neutralised with carbonate of lead; the filtered liquid decomposed by hydrosulphuric acid; and the filtrate evaporated, first over the water-bath, afterwards in vacuo. (Deville.)

*Properties.* Small white crystalline laminæ. (Deville.)

| | | | | Deville. |
|---|---|---|---|---|
| 14 C | 84 | 44·22 | | 44·35 |
| 10 H | 10 | 5·27 | | 5·35 |
| 2 S | 32 | 16·82 | | |
| 8 O | 64 | 33·69 | | |
| $C^{14}H^{8}S^{2}O^{6}$ + 2Aq | 190 | 100·00 | | |

*Decompositions.* Blackens quickly when dried over oil of vitriol in vacuo. When heated, it yields sulphurous acid, empyreumatic products and charcoal.

*Combinations.* The acid quickly absorbs moisture from the air.

The *sulphotoluates* do not suffer much alteration by exposure to the air; Their solution does not precipitate nitrate of copper or nitrate of silver.

*Sulphotoluate of Ammonia* crystallises pretty readily in stellate needles. (Deville.)

*Sulphotoluate of Potash.* — Indistinctly crystalline laminæ containing 15·3 p. c. potash and no water. [The formula $C^{14}H^{7}K,2SO^{3}$ requires 22·55 per cent. of potash; the formula $C^{14}H^{7}K,2SO^{3}$ requires 15·72 p. c. potash. L.] Very soluble. (Deville.)

*Sulphotoluate of Baryta.* — Obtained by saturating the solution of toluol in fuming sulphuric acid with carbonate of baryta; the solution yields anhydrous crystalline scales. (Deville.)

| | | | | Deville. |
|---|---|---|---|---|
| Ba | 68·6 | 28·63 | | 28·40 |
| 14 C | 84·0 | 35·06 | | 34·43 |
| 7 H | 7·0 | 2·92 | | 3·16 |
| 2 S | 32·0 | 13·36 | | 13·80 |
| 6 O | 48·0 | 20·03 | | 20·21 |
| $C^{14}H^{7}Ba,2SO^{3}$ | 239·6 | 100·00 | | 100·00 |

Does not deliquesce on exposure to the air. Dissolves very easily in water. (Deville.)

The *lead-salt* is very soluble in water.

*Secondary Nuclei of Toluene.*

*Oxygen-nucleus* $C^{14}H^{6}O^{2}$. *Salene.*

## Saliretin. $C^{14}H^{8}O^{2}$.

Braconnot. (1831.) *J. Chim. méd.* 7, 17; *Pogg.* 20, 621.
Piria. *Ann. Pharm.* 29, 300; *Compt. rend.* 7, 935; *J. pr. Chem.* 16, 412. — *Ann. Pharm.* 30, 178 and 189; *Ann. Chim. Phys.* 69, 281; *J. pr. Chem.* 17, 241. — *Ann. Pharm.* 56, 45; *N. Ann. Chim. Phys.* 14, 268; *Pharm. Centr.* 1839, 370; 1845, 758.
Liebig. *Ann. Pharm.* 30, 186; *Pharm. Centr.* 1839, 468.
Gerhardt. *N. Ann. Chim. Phys.* 7, 215; *Rev. scient.* 10, 216; *Pharm. Centr.* 1843, 169.
Roser. *Ann. Pharm.* 74, 184.

*Formation.* By the action of most acids, even in the very dilute state, on saligenin or salicin. (Piria, Braconnot.) By treating an alcoholic solution of salicin with chlorine gas. (Roser.)

*Preparation.* Salicin or saligenin is treated for some time with dilute sulphuric or hydrochloric acid. — The saliretin collects on the surface of the liquid. The more dilute the acid, the purer and whiter is the product; when salicin is used, glucose remains in solution. (Piria.) Concentrated sulphuric or hydrochloric acid converts salicin into a resin, which, on addition of water, is deposited in the form of a white powder. (Braconnot.) The decomposition of salicin by dilute acids takes a very long time and is not easily completed, so that the quantity of sugar obtained is very variable. (Roser.) — Gerhardt dissolves the precipitated saliretin in alcohol and precipitates it with water.

*Properties.* Resinous, white, often somewhat yellowish. Fusible. It can only be dehydrated by long continued heating in a current of dry air, and it is only when it has become perfectly transparent that its weight remains constant.

| | | | Piria. | | Gerhardt. |
|---|---|---|---|---|---|
| | | | *a.* | *b.* | |
| 14 C | ·84 | 79·24 | 68·58 | 72·95 | 76·5 |
| 6 H | 6 | 5·65 | 5·91 | 5·79 | 6·3 |
| 2 O | 16 | 15·11 | 25·51 | 21·26 | 17·2 |
| $C^{14}H^6O^2$ | 106 | 100·00 | 100·00 | 100·00 | 100·0 |

The formula $C^{14}H^6O^2$, which represents saliretin as isomeric with bitter almond oil and benzoïn, is adopted by Piria, because, in the action of dilute acids upon saligenin, the only product obtained besides saliretin, is a very small quantity of a bitter deliquescent substance; and the difference of 15·99 p. c. between the saligenin used and the saliretin obtained may be accounted for by the addition of 2 At. water (Calc. 14·52 p.c.). The two samples *a* and *b* formerly examined were probably not anhydrous (*Ann. Pharm.* 56, 46). [The analyses however exhibit, when compared with the calculated composition, an excess of hydrogen and oxygen in the ratio, not of 1·8 but of 1·12 (L.)]. Gerhardt suggested that the saliretin which he himself analysed was also not quite pure [the excess of hydrogen and oxygen which he found is in the ratio of 1 : 3·6 (L.)]; he more recently doubled the formula of saliretin, making it $C^{28}H^{12}O^4$ (*Traité*, 3, 310).

*Decompositions.* 1. By dry distillation, it yields carbolic acid, water and a residue rich in charcoal. (Gerhardt.) — 2. Boiled with *chlorate of potash* and *hydrochloric acid*, it does not yield chloranil, but a yellow amorphous mass, insoluble in water and alcohol. (Hofmann, *Ann. Pharm.* 52, 64.) — 3. Boiled with strong *nitric acid*, it first yields a yellow resin and red vapours, and ultimately forms a solution which appears to contain picric acid. (Piria, Gerhardt.) — 4. *Oil of vitriol* colours it blood-red. — 5. It does not yield salicylous acid when boiled with chromate of potash and sulphuric acid. (Piria.) — 6. It is insoluble in ammonia, but dissolves in aqueous fixed alkalis, whence it is precipitated as a white jelly by acids, even by carbonic acid. (Piria.)

Saliretin is insoluble in water, but dissolves in strong *acetic acid*, in *alcohol* and in *ether*, and is precipitated from its solution by water. (Piria.)

## Saligenin.

$C^{14}H^8O^4 = C^{14}H^6O^2,H^2O^2$.

PIRIA. (1845.) *N. Ann. Chim. Phys.* 14, 251; *Ann. Pharm.* 56, 53; *J. pr. Chem.* 36, 321; abstr. *Compt. rend.* 17, 186; *Pharm. Centr.* 1845, 569.—*Ann. Pharm.* 81, 245; *Pharm. Centr.* 1852, 151.

*Formation.* By the action of dilute acids or emulsin on salicin:

$$C^{52}H^{36}O^{28} + 4HO = 2C^{14}H^8O^4 + C^{24}H^{24}O^{24}.$$

According to Piria, it is contained in populin in conjunction with benzoic acid and glucose, but cannot be separated therefrom by dilute acids or by emulsin.

*Preparation.* An aqueous solution of salicin acidulated with sulphuric or hydrochloric acid is heated till it just boils up, the liquid then saturated with chalk, and the filtrate shaken with ether which takes up the saligenin. A considerable quantity of saliretin is always formed at the same time. — 2. When 50 pts. of finely pulverised salicin suspended in 500 pts. of water are shaken up with 3 pts. of Robiquet's emulsin, and heated in lukewarm water to a temperature not exceeding 40°, the salicin dissolves, being decomposed in the course of 24 hours into glucose and saligenin. When no more than the prescribed quantity of water is employed, part of the saligenin crystallises out; and if the liquid be then twice shaken up with an equal bulk of ether, and the ethereal liquid evaporated over the water-bath, the residue solidifies in a white mass composed of pearly laminæ, which may be pressed between paper and repeatedly crystallised from boiling water: If almond-milk is used instead of emulsin, the ether likewise extracts an oil, and the product obtained by evaporation is impure and more or less coloured. The emulsin is likewise coagulated by the ether.

*Properties.* White rhombic tables having a pearly lustre, or small colourless rhombohedrons. By spontaneous evaporation of the aqueous solution, there is formed a white opaque mass composed of microscopic, shining, iridescent laminæ. Saligenin is unctuous to the touch. In vacuo over oil of vitriol, it does not give off water, but partly volatilises, in consequence of which the oil of vitriol becomes covered with a crimson crust. — Melts when heated, forming a colourless, transparent liquid, which solidifies in a crystalline crust at 82°. When heated for some time to 100°, it yields a sublimate of delicate, white, shining, iridescent laminæ. — The aqueous solution imparts a bright indigo colour to ferric salts.

| | | | Piria. |
|---|---|---|---|
| 14 C | 84 | 67·74 | 67·47 |
| 8 H | 8 | 6·45 | 6·62 |
| 4 O | 32 | 25·81 | 25·91 |
| $C^{14}H^8O^4$ | 124 | 100·00 | 100·00 |

The alcohol of the salene-series.

*Decompositions.* 1. Saligenin heated above 100°, gives off aqueous vapour and salicylous acid. Between 140° and 150°, it becomes very viscid, and solidifies on cooling, in a mass which is less crystalline the more strongly it has been heated, and at length there is formed an amber-coloured, translucent resin having the properties of saliretin. — 2. Exposed to the air in contact with platinum black, it is quickly converted into salicylous acid; at higher temperatures, the same conversion is produced by mere contact with the air, or by chromic acid, oxide of silver, &c., without the formation of any other organic substance or of carbonic acid;

$$C^{14}H^8O^4 + 2O = C^{14}H^6O^4 + 2HO.$$

Mercuric oxide does not act upon saligenin. — When saligenin is heated with sulphuric acid and peroxide of manganese, carbonic acid and formic acid are produced, without a trace of salicylous acid. — 3. *Chlorine gas* acts violently on dry saligenin, giving off hydrochloric acid and forming a yellow resin, which gradually turns red, and ultimately solidifies in a mass composed of small crystals, which melt and turn red when exposed to the further action of chlorine. *Bromine* acts in a similar manner. — The chief product formed by the action of chlorine gas on a concentrated aqueous solution of saligenin, is terchlorocarbolic acid (xi, 182). — 4. With *iodine* and *phosphorus*, saligenin forms a brown liquid which appears to contain $C^{14}H^6O^2,IH$, but is very unstable (Limpricht, private communication). — 5. Saligenin heated with *dilute acids*, is resolved into saliretin and water : $C^{14}H^8O^4 = C^{14}H^6O^2 + 2HO$. — In the decomposition by hydrochloric acid, the liquid filtered from the saliretin yields by evaporation only 0·6 per cent. of a hard, very bitter, deliquescent extract, probably resulting from the action of the hydrochloric acid on the saliretin previously formed. — 6. Hot concentrated *nitric acid* decomposes saligenin, giving off nitrous vapours and carbonic acid and forming picric acid. Dilute nitric acid at ordinary temperatures colours saligenin dark red, and at the same time, small resinous drops rise to the surface of the liquid, and are increased by mixing it with water, the odour of salicylous acid also becoming perceptible. The liquid neutralised with carbonate of lime imparts a violet colour to ferric salts, and yields by distillation a milky water, which smells of salicylous acid, but likewise deposits small yellow needles. — 7. *Oil of vitriol* dissolves saligenin with deep red colour. — 8. Saligenin is not decomposed by *potash-ley*. When fused with hydrate of potash, it gives off hydrogen, and the residue contains salicylate of potash. — 9. The solution in aqueous *ammonia* acquires, in the course of a few hours, a green colour which is changed to rose-red by acids, and restored by alkalis; it disappears on boiling, and reappears as the solution cools.

9. Saligenin is attacked by *chloride of benzoyl*, with formation of hydrochloric acid vapours, a compound $C^{14}H^7O^2,C^{14}H^5O^2$, analogous to the compound ethers, appearing to form (Limpricht, private communication).

Saligenin dissolves in 15 pts. of water at 22°, and in nearly all proportions of boiling water.

It dissolves in ammonia. It appears to combine with potash, inasmuch as no more saligenin can be extracted from the aqueous solution, after the addition of a drop of potash-ley. Aqueous saligenin does not precipitate the solutions of baryta-salts, lime-salts, neutral acetate of lead, copper-salts, corrosive sublimate, nitrate of silver or tartar-emetic; in basic acetate of lead, it forms a scanty precipitate of variable compo-

sition. Ferric salts impart to the aqueous solution of saligenin a bright indigo-colour, which is rapidly destroyed by heating or by the action of chlorine or of acids. The alcoholic and ethereal solutions do not exhibit this colouring.

Saligenin dissolves readily in *alcohol* and in *ether*.

## Salicylous Acid.

$$C^{14}H^{6}O^{4} = C^{14}H^{6}O^{2},O^{2}.$$

PAGENSTECHER. (1834.) *Repert.* 49, 337; 51, 364; *Ann. Chim. Phys.* 69, 331; *Pharm. Centr.* 1835, 137.
LÖWIG. *Pogg.* 36, 383; *Pharm. Centr.* 1836, 58.
PIRIA. *Compt. rend.* 6, 620; 7, 935; *Ann. Pharm.* 29, 300; *J. pr. Chem.* 14, 285; 16, 412.—Further: *Ann. Pharm.* 30, 153; *Ann. Chim. Phys.* 69, 281; *J. pr. Chem.* 17, 241; *Pharm. Centr.* 1839, 370.
DUMAS. *Compt. rend.* 7, 940; *Ann. Chim. Phys.* 69, 326; *Ann. Pharm.* 29, 306; *J. pr. Chem.* 16, 418; *Pharm. Centr.* 1839, 375.
LÖWIG & WEIDMANN. *Pogg.* 46, 57; *Pharm. Centr.* 1839, 129.
ETTLING. *Ann. Pharm.* 29, 309; 35, 241; 53, 77; *Pharm. Centr.* 1839, 376; 1840, 837; 1845, 324.
WÖHLER. *Ann. Pharm.* 39, 121.
MARCHAND. *J. pr. Chem.* 26, 394; *Pharm. Centr.* 1842, 885.
BERTAGNINI. *Ann. Pharm.* 85, 193.
PIRIA. *Ann. Pharm.* 81, 245; *Pharm. Centr.* 1852, 151.

*Salicylige Säure, Ulmarsäure, Spiräaöl, Spiräa-saure, Spiroylige Säure, Salicylwasserstoff, Acidum spirosum, Hydrure de Salicyle.*

*Sources.* In the flowers of *Spiræa ulmaria* (Pagenstecher);—according to Pagenstecher, however, it cannot be extracted by alcohol and appears to be formed by the action of water (Dumas; compare also Buchner, *N. Repert.* 2, 1);—also in the haulm, especially of the double variety, and the rootstock of *Spiræa ulmaria;* in the haulm of *Spiræa digitata, lobata* and *filipendula;* but not in the shrubby spiræas (Wicke, *Ann. Pharm.* 91, 374); in the warty secretion of the larvæ of *Chrysomela populi* (Liebig, Schweizer, *N. Repert.* 2, 1; 3, 212).

*Formation.* 1. By the dry distillation of kinic acid. (Wöhler.)—2. By the oxidation of saligenin, either in the free state, or as contained in salicin or populin; therefore by the action of chromate of potash and sulphuric acid (Piria), or of aqueous osmic acid (Buttlerow, *J. pr. Chem.* 56, 278), on saligenin, salicin or populin, or by the action of bromine or iodine on salicin in water containing potash. (Lefert.)—3. By the fermentation of salicin. (Ranke, *J. pr. Chem.* 56, 1.)—4. In the decomposition of helicin by fermentation, by acids, or by heating with alkalies.

*Preparation. a. From the flowers of Spiræa ulmaria.*—1. The dry flowers are distilled with a sufficient quantity of water, till a quantity of liquid has passed over equal to the weight of the flowers, and the transparent, colourless, strong-smelling distillate is redistilled till $\frac{1}{8}$ has passed over. The second yellowish distillate, at the bottom of which are numerous oil-drops, is neutralised with lime-water and two-thirds

distilled off, and the residue is mixed with sulphuric acid and distilled; the liquid which then passes over, exhibits the same characters as the second distillate, excepting that its odour is purer and milder. (Pagenstecher.) The oil obtained by Pagenstecher is a mixture of two or three bodies, which solidifies completely at — 22° or — 23°. Between — 18° and — 20°. it deposits, after some weeks, large transparent crystals of salicylous acid, which melt at ordinary temperatures; it likewise contains a camphor which crystallises in pearly scales and remains solid at ordinary temperatures, and an indifferent oil which passes over when the mixture is distilled with potash-ley of sp. gr. 1·28. (Ettling.) — 2. The water distilled off, with cohobation, from the flowers of *Spiræa ulmaria* is repeatedly shaken up with ether; the decanted ether agitated with potash; and the potash-solution supersaturated with phosphoric acid and distilled. At first salicylous acid passes over, and afterwards salicylic acid sublimes in long needles. (Löwig & Weidmann.) — 3. The dried flowers are distilled with water till the distillate is no longer coloured yellow by potash: the distilled liquid is then neutralised with potash (or with carbonate of potash, as directed by Berzelius in his *Lehrbuch*) and evaporated nearly to dryness in a distillatory apparatus, to keep out the air. The residue is slightly supersaturated with phosphoric acid and distilled, and the salicylous acid which passes over, partly as aqueous solution, partly in oil-drops, is purified as in the second method, dried over chloride of calcium, and distilled. (Löwig, *Lehrb.* 2, 747.) — *b. From Salicin.* — 1. Salicin is dissolved in 6 pts. of hot water contained in a tubulated retort, and an aqueous solution of 4 pts. of chromate of potash mixed with 3 pts. of oil of vitriol, is added in small portions through the tubulure. At each addition, a brisk action takes place, the mixture becomes green, and water passes over containing suspended globules of salicylous acid. (Piria.) An intimate mixture of 2 pts. salicin and 2 pts. chromate of potash, is shaken up in a retort with 16 pts. of water, and a mixture of 3 pts. of oil of vitriol and 8 pts. water then added. A slight evolution of gas takes place, lasting for half or three quarters of an hour, the liquid at the same time becoming heated to between 60° and 70°, and assuming an emerald-green colour; it must then be gently heated, as long as drops of oil pass over. — 250 grms. of salicin yield about 60 grms. of salicylous acid. Towards the middle of the distillation, there is formed a brownish resin which floats on the water and amounts to about a fourth part of the salicin. With the proportions of material recommended by Piria, this resin is not produced; but on the other hand; the quantity of salicylous acid obtained is much less; if sulphuric acid is added to Piria's mixture after the distillation, an additional quantity of salicylous acid is obtained, amounting to not quite half the largest product. — The formation of the resin appears to be connected with a decomposition of the salicylous acid; if this acid be boiled with a mixture of sulphuric acid and chromate of potash in an apparatus which allows the condensed vapours to flow back again, a similar resin may be extracted from it by ether. (Ettling.) Marchand takes 3 pts. of salicin, 3 pts. of chromate of potash, 36 pts. of water and 4½ pts. of oil of vitriol, and after 20 pts. of liquid have passed over, adds 20 pts. more of water. — 2. A decoction concentrated as much as possible of willow-bark rich in salicin, is strained through linen and evaporated to a thin extract, which is then mixed with an adequate quantity of chromate of potash and sulphuric acid (2 pts. chromate of potash to 3 pts. oil of vitriol) and distilled as long as any oil passes over with the water. The

salicylous acid thus obtained is purified by combining it with an alkali, concentrating the solution by evaporation, and distilling with dilute sulphuric acid. (Wöhler.)

*Properties.* Colourless oil, which solidifies at — 20°, forming large transparent crystals. (Ettling.) Boils between 160° and 170° (Löwig & Weidmann), from 182° to 185° (Ettling), at 196·5, with the barometer at 0·76 met. (Piria.) Sp. gr. 1·173 at 13·5°. Vapour—density= 4·27. (Piria.) — Has a pleasant aromatic odour somewhat like that of bitter almonds (Piria); possesses in the highest degree the odour of the flowers of *Spiræa ulmaria.* (Löwig.) Its taste is burning and aromatic. — The aqueous solution first reddens litmus-paper and then decolorises it completely; litmus-paper is bleached by the vapour. (Löwig.) It does not redden litmus. (Pagenstecher, Ettling, Piria.) — The aqueous solution colours ferric salts violet.

| | | | Löwig. | Piria. | Löwig & Weidman. | Ettling. | Marchand. |
|---|---|---|---|---|---|---|---|
| 14 C | 84 | 68·85 | 66·17 | 68·37 | 69·28 | ..... | 68·89 | 68·65 |
| 6 H | 6 | 4·92 | 5·55 | 4·94 | 4·87 | ..... | 5·01 | 5·20 |
| 4 O | 32 | 26·23 | 28·28 | 26·69 | 25·85 | ..... | 26·10 | 26·15 |
| $C^{14}H^6O^4$ | 122 | 100·00 | 100·00 | 100·00 | 100·00 | ..... | 100·00 | 100·00 |

The acid aldide of the salene-series. It is regarded by Gerhardt as the hydride of salicyl, $C^{14}H^5O^4,H$, the external atom of hydrogen being replaceable by metals.

*Decompositions.* 1. The acid turns red when exposed to the *air*, but does not undergo any further change. (Piria.) It may be rendered colourless again by one distillation. (Gerhardt, *Traité* 3, 294.) It does not alter in oxygen-gas either moist or dry. (Löwig.) — 2. When vapour of salicylous acid is passed through a red-hot tube filled with platinum black, a dark viscid mass passes over, the greater part of which dissolves in potash, leaving a solid substance, which volatilises with the watery vapours, in the form of an oil which solidifies in needles, and has a peculiar agreeable odour like that of benzol. The same body is obtained in smaller quantity, when salicylous acid is distilled in the oil-bath with an equal weight of lime or baryta. (Anderson, *N. Ed. Phil. J.* 41, 298.) — 3. The acid burns with a bright sooty flame. (Löwig.) — 4. With dry *chlorine*, it becomes heated and gives off chlorosalicylous and hydrochloric acids. (Löwig, Piria, Ettling.) Chlorine gas passed into the second distillate obtained from the flowers of *Spiræa ulmaria* (p. 235), first renders it turbid, and afterwards causes it to deposit delicate white laminæ, which are coloured yellow by a greater quantity of chlorine. On decanting the reddish water from the precipitate, the latter is seen to consist of a red, viscid, strong-smelling substance and white crystals. (Pagenstecher, Löwig & Weidmann, Ettling; vid. *chlorosalicylous acid.*) — Chlorine-gas passed through oil of spiræa, colours it violet at first; but the colour soon disappears and crystals of chlorosalicylous acid are formed. (Dumas.) — When chlorine gas is passed through salicylous acid shaken up with warm water, the acid first becomes solid, then liquid again and yellowish red; when set aside overnight, it solidifies into a light scarlet, crystallo-granular mass, which when pressed with paper, gives up to the paper a scarlet oil, while a crystalline mass of lighter colour remains behind (v. *chlorosalicylous acid*). The water from which the crystals have been deposited contains a large quantity of hydrochloric acid, and after a while deposits yellowish crystalline laminæ [of chloranil? L.]. (Ettling.)

— 5. The oily acid treated with vapour of *bromine* or with bromine-water, yields bromosalicylous acid, or by longer action, bibromosalicylous acid (Löwig & Weidmann, Heerlein); in sunshine, with the aid of heat and renewal of the bromine as it evaporates, a compound is formed, which is insoluble in potash, sparingly soluble in alcohol and ether, and does not unite with salifiable bases. (Löwig & Weidmann.) In this compound, Löwig & Weidmann found 19·1 p. c. carbon and 67·12 bromine, whence they supposed that it contains 3 At. bromine [the formula $C^{14}Br^3H^3O^4$ requires 23·4 carbon and 68·4 bromine. L.] The distillate from the flowers of *Spiræa ulmaria* becomes milky when mixed with bromine, loses nearly all its odour, and deposits white flakes which dissolve readily in alcohol and ether, and crystallise therefrom in yellowish needles having a rather strong odour of bromine. *Iodine* gradually colours it yellowish red and deposits a reddish oil without alteration of the odour. (Pagenstecher.) Salicylous acid dissolves iodine without decomposition. (Löwig, Piria.)

5. Salicylous acid moderately heated with *nitric acid* of ordinary strength and not in excess, forms nitrospiroylous acid. (Pagenstecher, Löwing & Weidmann.) — When it is treated with a cold mixture of nitric acid and oil of vitriol, a mixture of several nitro-compounds is produced. (Limpricht.) Fuming nitric acid acts very violently on salicylous acid, nitrous fumes being evolved, and a yellow viscid mass produced, which may be distilled and smells very much like fresh butter, tastes very bitter, and imparts a yellow colour to the skin, nails and saliva; when distilled with water, it passes over partly in solution, partly as a powder. The residue of the distillation yields by evaporation, transparent colourless prisms of an acid which detonates when heated. (Löwig.) — Salicylous acid heated for some time with nitric acid, yields picric acid and carbonic acid. (Piria.) When it is gently heated with moderately dilute nitric acid, red fumes are given off and salicylic acid is produced. (Löwig.) — 6. Boiled with hydrochloric acid and chlorate of potash, it yields chloranil and carbonic acid. (Hofmann):

$$C^{14}H^6O^4 + 10Cl + 4O = C^{12}Cl^4O^4 + 6ClH + 2CO^2.$$

6. When salicylous acid is continuously boiled with bichromate of potash, sulphuric acid, and water, in such a manner that the escaping vapours may be condensed and flow back again, there remains, after the distillation of the unaltered salicylous acid, a green residue, from which ether extracts a brown resin and salicylic acid. (Ettling.) — 8. Salicylous acid in contact with *oil of vitriol*, turns yellow and becomes covered with a crust (Ettling); it first turns brown and then black (Pagenstecher, Löwig). When vapours of anhydrous sulphuric acid are passed over dry salicylous acid, a neutral insoluble body is formed, which crystallises in large prisms, has the same composition as salicylous acid, and bears to that acid the same relation that benzoïn bears to bitter almond oil. (Piria.)

9. When salicylous acid is heated with *cupric oxide* or with cupric oxide and potash, salycilic acid and cuprous oxide are produced. (Ettling.) — 10. *Oxide of silver* is reduced by salicylous acid [and salicylic acid formed? L.] On mixing concentrated solutions of salicylite of potash and nitrate of silver, a yellow precipitate is formed, which soon turns grey and afterwards black; if the solution is very dilute, no precipitate is formed, but after 24 hours or immediately on heating, the sides of the vessel become silvered. (Ettling, Löwig & Weidmann.)—11. With gaseous or aqueous *ammonia*, salicylous acid forms salhydramide, $C^{28}N^2H^{18}O^6$.

(Ettling.)—Also with hydrosulphate of ammonia. (Laurent.)—12. Heated with excess of *hydrate of potash*, it first turns red-brown (rufin [v. *salicin*] being perhaps formed, according to Mulder), then becomes colourless and gives off a large quantity of hydrogen gas: the mass then contains salicylite of potash. (Piria.) — 13. Salicylite of potash exposed to the air in the moist state, becomes covered in a few minutes with green and afterwards with black specks, and gradually becomes black throughout; after three or four days, it is completely converted, with absorption of oxygen, into acetate and melanate of potash (xi. 163). (Piria.)

*Combinations.* Salicylous acid dissolves abundantly in water; the solution has the odour and taste of the acid, and imparts a violet-red colour to ferric salts, even when very dilute.

Salicylous acid dissolves readily in aqueous alkalis, with rise of temperature; in alkaline carbonates, with evolution of carbonic acid; if the solution is strong, the salt separates out.

The *Salicylites* or *Salicylides* generally contain only 1 At. of base, their formulæ being $C^{14}H^5MO^4$. The salicylites of the alkalis dissolve in water with tolerable facility; most of the others are insoluble. They are yellow and contain water of crystallisation. The solutions impart a violet-red colour to ferric salts. In the moist state they are quickly decomposed, emitting the odour of roses, and turning brown and ultimately black.

*Salicylite of Ammonia.* — The acid in the free state readily absorbs ammoniacal gas; the resulting compound contains 8·832 p. c. ammonia and 91·168 acid, numbers which correspond with 3 At. acid to 2 At. ammonia. (Ettling.)

*a. Normal.* — The oily acid covered with concentrated ammonia, is converted, with rise of temperature and considerable increase of bulk, into a light yellow, thick, pasty mass, which must be washed with cold alcohol. The salt crystallises from solution in hot alcohol, in delicate, light yellow, transparent needles united in tufts. It does not alter at 100°, melts like wax at 115°, and at a somewhat higher temperature, volatilises without decomposition in the form of a yellow smoke. (Pagenstecher, Löwig, Piria, Ettling.)

| | | | Löwig. |
|---|---|---|---|
| $NH^3$ | 17 | 12·23 | 13·52 |
| $C^{14}H^6O^4$ | 122 | 87·77 | 86·48 |
| $C^{14}H^5(NH^4)O^4$ | 139 | 100·00 | 100·00 |

With aqueous potash, it emits the odour of ammonia, but only after some time or on the application of heat. (Pagenstecher, Löwig, Ettling.) [On this account, it is regarded by Gerhardt (*Traité*, 3, 293) as salhydramide; nevertheless, according to Pagenstecher, Löwig & Ettling, acids immediately precipitate salicylous acid from it, and, according to Löwig and also Löwig & Weidmann, it decomposes with the metallic salts of the stronger acids into the ammonia-salt of the stronger acid and a salicyate of the metallic oxide. (L.)] — The alcoholic solution evaporated with excess of ammonia, yields golden-yellow needles of salhydramide. The yellowish white needles of salicylite of ammonia, which at first separate from an alcoholic solution of salicylous acid mixed with ammonia, dissolve spontaneously in five or ten minutes without rise of temperature, and in five or ten minutes more the liquid again becomes turbid and

deposits deep yellow crystals of salhydramide. (Ettling.) — The salt decomposes when exposed to the air or in vacuo, giving off ammonia and leaving salicylous acid. (Piria.) — In the moist state, it soon becomes black and semi-fluid, even in close vessels; giving off ammonia and exhaling the penetrating odour of oil of roses. (Löwig.)

It is insoluble in water, sparingly soluble in cold alcohol, abundantly in boiling alcohol.

*b. Acid.* — Obtained by dissolving *a* in warm water and adding salicylous acid; crystallises on cooling in slender yellow, transparent, aggregated needles. It dissolves in alcohol more readily than in water, remains unaltered at 100°, melts at 115°, and sublimes without alteration at a higher temperature. (Berzelius, *Lerhb.*, 4, 350.)

*Salicylous Acid with Bisulphite of Ammonia.* — An aqueous solution of bisulphite of ammonia, of 29° B. mixes readily and with rise of temperature, with an equal volume of salicylous acid, forming a yellow oily liquid which after a few hours, solidifies in a crystalline mass. The solution in a small quantity of warm water deposits, on cooling, faintly yellowish needles, which, when exposed to the air for a few days, solidify into a tough very bitter mass. (Bertagnini.)

*Salicylite of Potash.* — *a. Normal.* — Potassium dissolves in the aqueous acid, with evolution of hydrogen. (Löwig.) — 2. When salicylous acid is mixed with potash-ley of about 45° Bm. the whole solidifies in a yellow crystalline mass, which separates from the excess of potash-ley; it must be quickly pressed between bibulous paper, and dissolved in a small quantity of hot absolute alcohol, whence the salt crystallises on cooling. (Piria.) — 3. The acid is dissolved in three times its bulk of 50 per cent. alcohol, and caustic potash-solution added till the mass becomes solid; 1 vol. more of the same alcohol is then added, and the whole gently warmed till the solid mass is dissolved. The crystals which separate on cooling are washed with a small quantity of cold strong alcohol, whereby they are rendered lighter, then pressed between bibulous paper and immediately dried in vacuo over oil of vitriol. (Ettling.) — Small straw-coloured prisms. (Löwig.) Golden-yellow, square tables, with a pearly lustre and unctuous to the touch. (Piria, Ettling.) Alkaline reaction. The salt contains water of crystallisation which cannot be completely expelled. (Piria.) Assumes a dark straw-yellow colour at 100° and gives off 10·72 p. c. water (2 At.; calc. 10·17); and no more at 120°.

| | *At* 100°. | | Ettling. |
|---|---|---|---|
| KO | 47·2 | 29·60 | 28·33 |
| $C^{14}H^{5}O^{3}$ | 113·0 | 70·40 | |
| $C^{14}H^{5}KO^{4}$ | 160·2 | 100·00 | |

Decomposes quickly in the moist state, yielding melanic and acetic acids. — When heated, it decomposes with appearance of fire, but without separation of charcoal. (Löwig.) — Sparingly soluble in water.

*b. Acid.* — The free acid is added to the solution of *a* in hot alcohol, till a sample of the liquid on cooling no longer yields tables, but specular crystals; it is then left to cool slowly, and the resulting crystals are washed till the yellow colour disappears. — White needles united in tufts. (Ettling.)

| | *At* 100°. | | | Ettling. |
|---|---|---|---|---|
| KO | 47·2 | .... | 16·73 | ..... 17·57 |
| $C^{14}H^5O^3$ | 113·0 | .... | 83·27 | |
| $C^{14}H^6O^4$ | 122·0 | | | |
| $C^{14}H^5KO^4,C^{14}H^6O^4$ | 282·2 | .... | 100·00 | |

Somewhat less alterable than *a* in moist air; decomposes with water into the neutral salt which dissolves, and free salicylous acid. (Ettling)

*Salicylous acid with Bisulphite of Potash.* — 1. Salicylous acid shaken up with an aqueous solution of bisulphite of potash of 28° Bm. dissolves without colour, and the saturated solution solidifies in a few seconds, forming a white inodorous crystalline mass, which may be recrystallised from alcohol. — 2. Dry sulphurous acid gas is passed into a cold-saturated alcoholic solution of salicylite of potash at a temperature between 40° and 50°, till the yellow colour disappears. — If the liquid be then left at rest, it soon becomes filled with slender needles arranged in spherical groups. — White, with a pearly lustre, and a faint odour of salicylous acid. Dissolves abundantly in cold water, easily in warm alcohol, less easily in cold alcohol.

| | | | | Bertagnini. |
|---|---|---|---|---|
| KO | 47·2 | .... | 19·47 | ..... 19·62 |
| 14 C | 84·0 | .... | 34·71 | ..... 34·76 |
| 7 H | 7·0 | .... | 2·89 | ..... 3·10 |
| 2 S | 32·0 | .... | 13·22 | ..... 12·72 |
| 9 O | 72·0 | .... | 29·71 | ..... 29·80 |
| $C^{14}H^6O^4,KO,2SO^2$ + Aq | 242·2 | .... | 100·00 | ..... 100·00 |

When heated, it gives off sulphurous and salicylous acid, leaving a residue of sulphite of potash which afterwards changes to sulphate. The aqueous solution when heated, soon becomes turbid and deposits salicylous acid; heated with acids, or mixed even in the cold with alkalis or alkaline carbonates, it turns yellow and yields a salicylite. The solution takes up iodine at first without colouration; when it begins to show colour, the whole of the sulphurous acid is converted into sulphuric acid, and the salicylous acid is set free. With bromine, the solution forms sulphuric and bromosalicylous acids. (Bertagnini.)

*Salicylite of Soda.* — *Acid.* — Prepared like the potash-salt. Crystallises more readily than the latter in delicate white needles permanent in the air. — Gives off at 100° only 0·607 per cent., at 135° in vacuo, 4·036 per cent. altogether; and at 140°, at which temperature drops of oil are deposited, 4·35 per cent.

| | *Air-dried.* | | | Ettling. |
|---|---|---|---|---|
| NaO | 31 | .... | 11·27 | ..... 11·55 |
| $C^{14}H^5O^3$ | 113 | .... | 85·46 | |
| $C^{14}H^6O^4$ | 122 | | | |
| HO | 9 | .... | 3·27 | ..... 4·36 |
| $C^{14}H^5NaO^4,C^{14}H^6O^4$ + Aq | 275 | .... | 100·00 | |

| | At 135°. | | Ettling. |
|---|---|---|---|
| NaO | 31 | 11·65 | 12·05 |
| $C^{14}H^5O^3$ | 113 | 88·35 | |
| $C^{14}H^6O^4$ | 122 | | |
| $C^{14}H^5NaO^4,C^{14}H^6O^4$ | 266 | 100·00 | |

It does not turn yellow at 135°, but at a higher temperature, it yields a sublimate of oily drops. (Ettling.)

*Salicylous acid with Bisulphite of Soda.* — $C^{14}H^6O^4 + NaO,2SO^2$. — An aqueous solution of bisulphite of soda of 27° Bm. dissolves a small quantity of salicylous acid; with larger quantities a white crystalline pulp is formed after a little agitation, and if this mass be redissolved by heat in the mother-liquor, beautiful shining crystals are obtained which have a sulphurous and pungent taste, dissolve readily in pure water, and likewise dissolve with partial decomposition in boiling alcohol. (Bertagnini.)

*Salicylite of Baryta.* — Salicylous acid shaken up with baryta-water forms a yellow precipitate (Löwig & Weidmann); the salt crystallises on cooling from baryta-water saturated while hot with salicylous acid (Piria), and separates as a yellow powder on mixing salicylite of potash or ammonia with a concentrated solution of chloride of barium. (Löwig, Piria.) — Yellow needles which at 160° in a current of dry air, give off 8·8 p.c. water (2 At.; calc. 8·67). (Piria.)

| | At 100°. | | Löwig & Weidmann. | | Crystallised. | | | Piria. |
|---|---|---|---|---|---|---|---|---|
| Ba | 68·6 | 36·18 | 35·44 | | Ba | 68·6 | 33·04 | 32·98 |
| 14 C | 84·0 | 44·30 | 42·91 | | 14 C | 84·0 | 40·46 | 40·58 |
| 5 H | 5·0 | 2·64 | 3·01 | | 7 H | 7·0 | 3·37 | 3·41 |
| 4 O | 32·0 | 16·88 | 18·64 | | 6 O | 48·0 | 23·13 | 23·03 |
| $C^{14}H^5BaO^4$ | 189·6 | 100·00 | 100·00 | | + 2Aq | 207·6 | 100·00 | 100·00 |

Very sparingly soluble in water.

*Salicylite of Magnesia* is obtained by treating the aqueous acid with hydrate of magnesia, or by precipitating a concentrated solution of chloride of magnesium with salicylite of ammonia, in the form of a light yellow powder, nearly insoluble in water. (Löwig.)

*Salicylite of Zinc.* — The aqueous acid dissolves zinc with evolution of hydrogen. (Pagenstecher.) When the aqueous acid is shaken up with oxide of zinc, a yellow solution is obtained which when left to evaporate in vacuo, deposits a yellow powder; the same precipitate is also formed on mixing acetate of zinc with salicylite of ammonia. (Pagenstecher, Ettling.)

*Salicylite of Lead.* — Separates on mixing the aqueous or alcoholic solution of the acid with solution of neutral acetate of lead, with addition of ammonia, but only after a considerable quantity has formed; on heating the liquid, the precipitate redissolves and separates again on cooling in heavy granules of a deep yellow colour. The precipitate which forms in the cold is flocculent at first, but gradually also becomes somewhat

granular. (Ettling.) Formed on mixing solution of neutral acetate of lead with acid [? L.] salicylite of ammonia, as a light yellow precipitate insoluble in water. (Löwig & Weidmann.) After drying in the air, it does not contain any water.

| | | | | Ettling. | | | Löwig |
|---|---|---|---|---|---|---|---|
| | | | *a.* | *b.* | *c.* | | & Weidmann. |
| 2 PbO | 223·6 | 66·43 | 66·81 | 67·59 | 66·92 | | 65·67 |
| 14 C | 84·0 | 24·95 | | | | | 23·96 |
| 5 H | 5·0 | 1·49 | | | | | 1·71 |
| 3 O | 24·0 | 7·13 | | | | | 8·66 |
| $C^{14}H^5O^3,2PbO$ | 336·6 | 100·00 | | | | | 100·00 |

*a* was precipitated hot from basic acetate of lead; *b* cold; *c* from the neutral acetate by ammonia.

When the salicylous acid is in excess, deep yellow transparent crystals form in the precipitate (Ettling.) When the aqueous acid is shaken up with hydrated oxide of lead, and the mixture left to stand for some time, small, light yellow, shining laminæ form in them (Löwig).

*Ferrous Salicylite.* — Aqueous protochloride of iron forms a dark violet precipitate with salicylous acid on addition of ammonia. (Pagenstecher, Ettling.)

*Ferric Salicylite.* — Aqueous sesquichloride of iron mixed with salicylous acid acquires a fine dark cherry-red colour. (Pagenstecher, Ettling,), violet-red (Piria), without forming a precipitate. The colour does not alter when the air is excluded, but on exposure to the air it gradually disappears as the acid evaporates (Pagenstecher, Ettling); addition of acids or exposure to the air changes the colour to dirty yellow. (Piria.) Water which contains only $\frac{1}{67100}$ of ferric oxide and does not yield a perceptible blue colour with ferrocyanide of potassium, acquires a distinct violet colour on the addition of salicylous or salicylic acid. (A. Dolfuss.)

Hydrochlorate of *cuprous oxide* forms a light brown precipitate with the aqueous acid on addition of ammonia. (Pagenstecher, Löwig.)

*Cupric Salicylite.* — 1. Recently precipitated cupric oxide shaken up with an excess of the aqueous acid, acquires a grass-green colour, and after washing with a small quantity of alcohol, forms a light green powder. (Pagenstecher, Löwig, Piria.) — 2. When a solution of 1 vol. salicylous acid in 50 or 60 vol. alcohol, is mixed with an aqueous solution of cupric acetate, the liquid acquires an emerald-green colour, and forms after a few minutes a large number of shining crystals, which increase when the free acetic acid is neutralised with potash. (If the liquid were neutralised with ammonia, the slightest excess would give rise to the formation of nitride of salicyl and copper.) The crystals are washed with alcohol. (Ettling.). — 3. When a solution of cupric sulphate is mixed with salicylite of ammonia, a bulky, somewhat crystalline precipitate is formed, containing a small quantity of sulphuric acid. (Pagenstecher, Löwig.) — Large green shining crystals, from 0·5 mm. to 1 mm. in length, and exhibiting a blue-green colour when dry. (Ettling.) Light green powder, having the taste of copper, with a scarcely perceptible aromatic character.

| | | | Löwig. | Piria. | Dumas. | Löwig & Weidmann. | Ettling. |
|---|---|---|---|---|---|---|---|
| Cu | 31·8 | 20·81 | 22·88 | 20·21 | 21·5 | 21·32 | 20·41 |
| 14 C | 84·0 | 54·97 | 51·48 | 54·59 | 54·1 | | 54·81 |
| 5 H | 5·0 | 3·27 | 3·44 | 3·44 | 3·2 | | 3·35 |
| 4 O | 32·0 | 20·95 | 22·20 | 21·76 | 21·2 | | 21·43 |
| $C^{14}H^5CuO^4$ | 152·8 | 100·00 | 100·00 | 100·00 | 100·0 | | 100·00 |

When heated to 125°, it loses 3·022 per cent, the odour of the acid at the same time becoming perceptible. Becomes blackish green at 180°, then dark-brown, and acquires a dark kermes colour at 220°. At the same time that the brown colour appears, gas begins to go off, consisting of carbonic acid and carbonic oxide, and a mixture distils over, consisting of salicylous acid, and benzoate of salicylous acid, which may be separated by potash. The salicylous acid must be reproduced, inasmuch as the salt does not contain water; the solution contains also another body which causes it to assume a splendid scarlet colour when mixed with oil of vitriol, but cannot be separated by fractional distillation. The residue contains cuprous salicylate. At a higher temperature, a black-brown oil passes over, having an empyreumatic odour. (Ettling.) — Chlorine passed over the salt forms chloride of copper and chlorosalicylous acid. (Löwig.) — When the salt is heated with hydrate of potash, the whole of the salicylous acid is converted into salicylic acid. (Ettling.)

Insoluble in water and alcohol.

*Mercuric Salicylite.* — The ammonia-salt forms with a very strong solution of mercuric chloride, a bulky precipitate of a light straw-yellow colour. (Löwig.)

*Salicylite of Silver.*—Oxide of silver dissolves slightly in aqueous salicylous acid; and the yellow, bitter, metallic-tasting solution yields by evaporation in vacuo, a brown residue which detonates in the flame of a candle. The same phenomenon is exhibited by the undissolved portion of oxide, which also acquires a black-brown colour. (Pagenstecher & Löwig.) — Nitrate of silver forms with acid salicylite of potash, a light yellow precipitate, which becomes grey when pressed, and decomposes completely after a while; if the precipitate is heated with water, the decomposition takes place immediately and the vessel becomes covered with a speculum of silver. (Löwig & Weidmann.)

Salicylous acid mixes in all proportions with *alcohol* and *ether*.

## Benzoate of Salicylous Acid.

$$C^{28}H^{10}O^6 = C^{14}H^5O^3,C^{14}H^5O^3.$$

Ettling. (1845.) *Ann. Pharm.* 53, 77.
Cahours. *Compt. rend.* 32, 62; *Ann. Pharm.* 78, 228.

*Parasalicyl, Benzoesaure salicylige Säure, Salicylure de benzoïle.*

*Formation.* 1. By the dry distillation of cupric salicylite. — 2. By the action of chloride of benzoyl on salicylous acid:

$$C^{14}ClH^5O^2 + C^{14}H^6O^4 = C^{28}H^{10}O^6 + HCl.$$

*Preparation.* 1. Air-dried salicylite of copper is subjected to distillation till the residue exhibits a uniform kermes-brown colour, and yields no more distillate at the same temperature; the oily distillate, in which crystals have already separated, is treated with potash-ley, which leaves undissolved the crystallised benzoate of salicylous acid, and likewise the portion which was dissolved in the oil; and the compound is crystallised from warm alcohol or ether. (Ettling.) — 2. Salicylous acid is treated with chloride of benzoyl. (Cahours.)

*Properties.* Colourless four-sided prisms belonging to the doubly oblique prismatic system, and obliquely bevelled. (Ettling, Cahours.) The largest crystals are obtained from the crude distillate. When obtained from the mother-liquor, they lose their lustre, and become coated with a white crust. (Ettling.) Melts at 127°, forming a pale yellow liquid, which solidifies in a radiated mass at about 98°. At 180°, it sublimes in long needles, undecomposed and without previous ebullition. (Ettling, Cahours.)

| | | | Ettling. |
|---|---|---|---|
| 28 C | 168 | 74·32 | 74·12 |
| 10 H | 10 | 4·42 | 4·52 |
| 6 O | 48 | 21·26 | 21·36 |
| $C^{28}H^{10}O^{6}$ | 226 | 100·00 | 100·00 |

Polymeric with benzoic anhydride and oreoselone.

*Decompositions.* The compound dissolves in hot strong nitric acid, nitrous vapours being given off and picric acid formed. (Ettling.)— 2. It is not decomposed by boiling with potash, either in aqueous or alcoholic solution, or even by fusion with hydrate of potash, under which circumstances indeed it volatilises. (Ettling). [? L.] — 3. It is not altered by cold oil of vitriol, but dissolves with yellowish red colour on the application of a gentle heat. If the liquid be strongly heated, it assumes a dingy red colour and gives off sulphurous acid; it may be mixed with water without turbidity, and yields a soluble salt with carbonate of baryta. (Ettling.) — 4. With chlorine or bromine in sunshine, it yields crystallised products. (Ettling.)

It is insoluble in water, but dissolves readily in *alcohol* and *ether*.

## ¶. Acetate of Salicylous Acid.

$C^{16}H^{8}O^{6} = C^{4}H^{3}O^{3},C^{14}H^{5}O^{3}$.

CAHOURS. *Compt. rend.* 44, 1252; *Ann. Pharm.* 104, 109.

*Acetosalicyl, Salicylure d'acetyle.*

Obtained by the action of chloride of acetyl ($C^{4}H^{3}O^{2}Cl$) on salicylous acid. On gently heating the mixture of the two substances, an energetic action takes place, hydrochloric acid is evolved, and acetate of salicylous acid is obtained in the form of a beautifully crystalline and perfectly neutral body.

Crystallises from the alcoholic solution in fine needles.

| | | | Cahours. |
|---|---|---|---|
| 18 C | 108 | 65·85 | 65·81 |
| 8 H | 8 | 4·78 | 4·85 |
| 6 O | 48 | 29·37 | 29·34 |
| $C^{18}H^8O^6$ | 164 | 100·00 | 100·00 |

Metameric with benzoic acetate or acetic benzoate (p. 96).

The compound is remarkably stable, scarcely undergoing any alteration when distilled over anhydrous baryta at a dull red heat. A portion thus treated yielded after distillation 66·05 p. c. carbon and 4·82 hydrogen. Neither is it altered by heating with solid hydrate of potash or with an alcoholic solution of potash. — *Chlorine, bromine,* and *fuming nitric acid* act upon it powerfully, forming crystalline products of substitution.

Insoluble in water, also in dilute aqueous ammonia or potash. Dissolves sparingly in cold, but more abundantly in hot alcohol. ¶.

## Salicylic Acid.

$C^{14}H^6O^6 = C^{14}H^4O^2,O^4$.

PIRIA. *Ann. Pharm.* 30, 165; *Ann. Chim. Phys.* 69, 296; *J. pr. Chem.* 17, 241; *Pharm. Centr.* 1839, 373.—Further: *Ann. Pharm.* 93, 262; *Pharm. Centr.* 1839, 378.

LÖWIG & WEIDMANN. *J. pr. Chem.* 19, 236; further: *Pogg.* 46, 83.

MARCHAND. *J. pr. Chem.* 26, 395; *Pharm. Centr.* 1842, 885.

PROCTER. *N. J. Pharm.* 3, 275; *J. pr Chem.* 29, 467; *Ann. Pharm.* 48, 66; *Pharm. Centr.* 1843, 699.

DELALANDE. *N. Ann. Chim. Phys.* 6, 346; *Ann. Pharm.* 45, 336; *Pharm. Centr.* 1843, 121.

GERHARDT. *N. Ann. Chim. Phys.* 7, 217; *Rev. scient.* 10, 207; *Ann. Pharm.* 45, 21; *Pharm. Centr.* 1843, 167.

CAHOURS. *Compt. rend.* 16, 853; 19, 423; *N. Ann. Chim. Phys.* 10, 327; 13, 90 and 113; *Ann. Pharm.* 52, 340; *Pharm. Centr.* 1843, 697.

ETTLING. *Ann. Pharm.* 53, 77; *Pharm. Centr.* 1845, 824.

SCHLIEPER. *Ann. Pharm.* 59, 26.

*Salicylsäure, Spirsäure, Spiroylsäure, Acide salicylique, spiroylique, hyperspiroylique.*

*Sources.* In the flowers of *Spiræa ulmaria.* (Löwig & Weidmann.) As methylsalicylic acid in *Gaultheria procumbens.*

*Formation.* 1. From salicylous acid by oxidation with aqueous chromic acid (Ettling, p. 338), or by heating with oxide of copper (Ettling, Piria.) — 2. By melting salicylous acid or salicin with hydrate of potash (Piria):

$$C^{14}H^6O^4 + KO,HO = C^{14}H^5KO^6 + 2H.$$

3. By heating indigo with hydrate of potash to 300°. The experiment does not always succeed; if the heat be not continued long enough, only anthranilic acid is

produced; if too long, a brown substance is formed. (Cahours.) — 4. By heating benzoate of copper. (Ettling.) — 5. By the action of nitrous acid on anthranilic acid (Gerland):

$$C^{14}NH^7O^4 + NO^3 = C^{14}H^6O^6 + 2N + HO.$$

6. Cumaric acid fused with hydrate of potash yields salicylite and acetate of potash. (Delalande):

$$C^{18}H^6O^6 + 2KHO^2 = C^{14}H^5KO^6 + C^4H^3KO^4 + 2H.$$

*Preparation.* — *a.* From the flowers of *Spiræa ulmaria.* — 1. The flowers are exhausted with ether; the ethereal solution distilled; the residue treated with water, which dissolves salicylic acid and tannin; and the aqueous solution is neutralised with carbonate of potash, evaporated and distilled with hydrochloric acid. The watery distillate slowly evaporated yields colourless needles. (Löwig & Weidmann.) — 2. The water distilled from the flowers, with frequent cohobation, is shaken up with ether; the decanted ethereal solution agitated with potash; and the alkaline solution distilled with sulphuric acid. At first salicylous acid passes over, but at last salicylic acid sublimes in long needles. (Löwig and Weidmann, *Pogg.* 46, 83.)

*b.* From oil of *Gaultheria* (*Wintergreen*). — 1. The oil is heated with strong potash-ley till no more wood-spirit is given off from it, and the residue precipitated with hydrochloric acid. The precipitate is washed with cold water and crystallised from hot alcohol. (Cahours.)

*c. From Salicylous acid, or from Salicin.* — 1. Hydrate of potash is heated in a silver basin, and as soon as it is melted, salicin is added by small portions, with continually stirring, whereupon the mass turns brown, swells up and gives off a large quantity of hydrogen. It is then heated as long as hydrogen is given off in presence of excess of potash. If the potash is not in excess, only a small quantity of salicylic acid is obtained, but instead of it, salicylous acid and a brown resinous substance which it is difficult to convert into salicylic acid, even by repeated fusion with hydrate of potash. If the process be rightly conducted, the mass becomes nearly colourless, exhibiting only a slight yellowish tint. According to Marchand, the mass first becomes deep yellow, then of a fine scarlet, then greenish yellow, and at last nearly white. If the heat be too strong, the mass blackens and gives off carbolic acid. The mass is dissolved in water; the solution supersaturated with hydrochloric acid, the vessel being surrounded with cold water; and the resulting crystalline mass is separated from the mother-liquor (which contains oxalic acid), and recrystallised from hot water. (Piria, Gerhardt, Marchand.) — 2. Cupric salicylite is heated in a retort till nothing more escapes at 220°, and the residue has assumed a uniform kermes-brown tint. This residue, consisting of cuprous salicylite, is then introduced into a glass tube and sulphuretted hydrogen passed over it, whereupon the mass becomes heated and blackened, and salicylic acid sublimes; and in order that the sublimate may not cover up the undecomposed mass and so protect it from further decomposition, it must be driven forward by the application of a gentle heat. Or the cuprous salicylite is dissolved in warm acetic acid, or in hydrochloric acid diluted with an equal quantity of water; the colourless liquid precipitated by sulphuretted hydrogen; and the liquid filtered from the sulphide of copper is evaporated to the crystallising point. Or, the solution of the copper-salt in acetic acid is supersaturated with ammonia, and precipitated with neutral acetate of lead; the preci-

pitate suspended in hot water; sulphuretted hydrogen passed through the liquid; and the sulphide of lead removed by filtration: the filtrate on cooling yields pure salicylic acid. (Ettling.)

*d. From Indigo* (comp. p. 246).—If the required temperature is exceeded, the salicylic acid decomposes and a brown substance is formed; if the heating is not continued long enough, nothing but anthranilic acid is produced.

*Properties.* Crystallises by spontaneous evaporation of the alcoholic solution in large oblique four-sided prisms. From a hot aqueous solution it separates on cooling in slender needles often an inch long. Particularly large and fine crystals are obtained by slow evaporation of the ethereal solution. (Cahours.) The crystals belong to the oblique prismatic (monoclinometric) system. (Marignac, *Liebig & Kopp's Jahresber*, 1855, 484.) — Melts at 158° (Cahours), at 121° (Procter), at 125° (Ettling). Sublimes at about 200°, without boiling, in slender needles having a strong lustre, and when pure may be completely distilled by careful heating. (Cahours, Ettling.) Has a sweetish sour taste, and produces irritation in the throat. Reddens litmus rather strongly. The aqueous solution imparts an intense violet colour (blood-red, according to Löwig & Weidmann) to ferric salts.

| | | | Piria. | Marchand. | Delalande. | Gerhardt. |
|---|---|---|---|---|---|---|
| 14 C | 84 | 60·87 | 60·34 | 60·44 | 60·41 | 60·91 |
| 6 H | 6 | 4·35 | 4·42 | 4·64 | 4·50 | 4·52 |
| 6 O | 48 | 34·78 | 35·24 | 34·92 | 35·09 | 34·37 |
| $C^{14}H^6O^6$ | 138 | 100·00 | 100·00 | 100·00 | 100·00 | 100·00 |

| | Cahours. *a.* | Cahours. *b.* | Ettling. | Gerland. |
|---|---|---|---|---|
| C | 60·76 | 60·83 | 60·80 | 60·32 |
| H | 4·41 | 4·37 | 4·51 | 4·28 |
| O | 34·83 | 34·80 | 34·69 | 35·40 |
| | 100·00 | 100·00 | 100·00 | 100·00 |

The acid analysed by Piria was prepared from salicylous acid; that examined by Marchand and by Gerhardt, from salicin; and that analysed by Delalande, from cumarin by fusion with hydrate of potash. Ettling analysed the acid obtained by heating cupric salicylite. The acid examined by Cahours was prepared from oil of wintergreen, *a* crystallised from alcohol, *b* obtained by sublimation: Gerland's acid was prepared from anthranilic acid.

*Decompositions.* 1. Salicylic acid when quickly heated, especially if it be impure, yields hydrate of phenyl. (Marchand, Cahours.) Heated with pounded glass or quick lime, it is resolved into hydrate of phenyl and carbonic acid (Gerhardt);

$$C^{14}H^6O^6 = C^{12}H^6O^2 + 2CO^2.$$

¶. The hydrate of phenyl thus prepared differs in some respects from that which is obtained by fractional distillation from coal-tar creosote. It crystallises with greater facility and does not deliquesce so quickly on exposure to the air. Moreover it yields different products with pentachloride of phosphorus. Hydrate of phenyl from coal-tar creosote yields with pentachloride of phosphorus, chloride of phenyl and triphenylic phosphate, $P(C^{12}H^5)^3O^8$, as determined by Williamson & Scrugham (xi, 173; see also *Chem. Soc. Qu. J.* 7, 240). But hydrate of phenyl from salicylic acid yields, when thus treated, not a triphenylic but a biphenylic phosphate or *biphenylophosphoric*

*acid* $P(C^{12}H^5)^2,H,O^8$, containing 1 At. of hydrogen replaceable by metals. This body resembles Scrugham's phosphate in distilling at a temperature much above the range of the mercurial thermometer, but differs from it in many other respects. It crystallises much more readily, and after being freed from adhering oil by pressure between paper, may be kept in paper during the warmest and dampest weather without alteration. It dissolves in a weak solution of caustic soda to which a little alcohol is added, forming the *biphenylophosphate of sodium* $P(C^{12}H^5)^2NaO^8$, which crystallises in well defined prismatic crystals containing 9 atoms of water. This salt is very efflorescent and dissolves readily both in water and in alcohol. On mixing the aqueous solution with neutral acetate of lead, a nacreous crystalline precipitate is formed, which appears to contain $P(C^{12}H^5)^2PbO^8$ (H. Watts: unpublished experiments). ¶.

Salicylic acid heated to 250° with fusel-oil in a sealed glass tube, is resolved into carbonic acid and hydrate of phenyl, while the fusel-oil remains unaltered. (Schlieper.) — 2. By the action of *bromine* or *chlorine*, 1, 2 or 3 At. hydrogen in the acid are replaced. With a small quantity of bromine, bromosalicylic acid, $C^{14}BrH^5O^6$, is produced; with excess of bromine, bibromosalicylic acid $C^{14}Br^2H^4O^6$; and if the action is aided by sunshine, terbromosalicylic acid, $C^{14}Br^3H^3O^6$, is formed after some time. — When the quantity of *chlorine* is such that part of the salicylic acid remains unaltered, chlorosalicylic acid, $C^{14}ClH^5O^6$ is formed; with excess of chlorine, the product is bichlorosalicylic acid, $C^{14}Cl^2H^4O^6$. No attempt was made to prepare terchlorosalicylic acid with the aid of sunlight. (Cahours.) When chlorine is passed into salicylate of potash, a green body separates consisting of impure bichlorosalicylate of potash; and when the brown liquid separated from this substance is saturated with chlorine, a yellowish-red substance is deposited containing bichlorosalicylic and terchlorocarbolic acids. (Cahours.) — 3. With *pentachloride of phosphorus*, the acid yields hydrochloric acid, the oily body which was regarded by Chiozza as chloride of benzoyl and hydrogen, and by Gerhardt as chloride of chlorobenzoyl, and leaves a carbonaceous residue (p. 116). — 4. The acid gently heated with *dilute nitric acid* gives off but a small quantity of gas, and is converted in a few seconds into nitrosalicylic acid. (Marchand.) *Fuming nitric acid* or a mixture of fuming nitric acid and oil of vitriol, acts violently in the cold and forms nitrosalicylic acid. (Gerhardt, Cahours.) When salicylic acid is heated with fuming nitric acid or with the mixture of nitric and oil of vitriol, a violent action takes place, resulting in the formation of picric and carbonic acids. (Gerhardt, Cahours.) — 5. Salicylic acid heated with *hydrochloric acid and chlorate of potash*, yields chloranil. (Hofmann, Cahours.) — 6. With the vapour of anhydrous sulphuric acid, it forms a gum soluble in water, which is *sulphosalicylic acid*, and combines with most bases, forming salts which dissolve readily in water. (Cahours.) — 7. Boiled with dilute sulphuric acid and peroxide of manganese, it yields formic acid. (Cahours.) — 8. The acid is not altered by a day's contact with fusel-oil; distilled with amylosulphate of potash, it is resolved into carbonic acid and hydrate of phenyl. (Schlieper.)

*Combinations.* The acid dissolves sparingly in cold, abundantly in hot water. It expels carbonic acid from its salts.

Salicylic acid is bibasic, forming principally neutral salts = $C^{14}H^4M^2O^6$ and acid salts = $C^{14}H^5MO^6$. It was formerly regarded as monobasic, the salts here considered as acid being then regarded as neutral; indeed the existence of salicylates containing 2 At. metal in place of hydrogen was not known till 1855, when several of them were prepared by Piria. Moreover, the compound $C^{14}NH^7O^4$, formerly regarded as salicylamide $N\left\{\begin{matrix}C^{14}H^5O^4\\H\\H\end{matrix}\right.$, the amide of the monobasic acid $\left.\begin{matrix}C^{14}H^5O^4\\H\end{matrix}\right\}O^2$,

has lately been shown by Limpricht to exhibit rather the characters of an amidogen-acid, viz., salicylamic acid $\left.\begin{matrix}NH^2(C^{14}H^4O^2)\\H\end{matrix}\right\}O^2$, (the radical $C^{14}H^4O^2$ being equivalent to $H^2$), being converted at a high temperature into salicylimide $N\left\{\begin{matrix}C^{14}H^4O^2\\H\end{matrix}\right.$: now it is only polybasic acids that form amidogen-acids and imides. The existence of acid ethers of salicylic acid, *e.g.*, methylosalicylic acid $\left.\begin{matrix}C^{14}H^4O^2\\(C^2H^3),H\end{matrix}\right\}O^4$ is also in favour of this view. On the nucleus-theory adopted in this handbook, the formula of salicylic acid regarded as a bibasic acid should be $C^{14}H^6,O^6$, and accordingly, the acid should take its place in the benzylene-series, next to benzoic acid $C^{14}H^6,O^4$.

The aqueous solutions of the alkaline salicylates turn brown on exposure to the air, a brown substance being formed which remains dissolved in the alkali. Most salicylates, when subjected to dry distillation, yield hydrate of phenyl and a carbonate.

*Salicylate of Ammonia.* — When the acid is saturated with ammonia, and the liquid boiled and evaporated, crystalline scales separate as it cools; by spontaneous evaporation of the diluted solution, silky needles are obtained. (Cahours, Procter.) Melts at 126°. (Procter.)

| | *Air-dried.* | | | Cahours. |
|---|---|---|---|---|
| 14 C | 84 | | 54·19 | 54·06 |
| N | 14 | | 9·03 | 8·94 |
| 9 H | 9 | | 5·81 | 6·02 |
| 6 O | 48 | | 30·97 | 30·98 |
| $C^{14}H^5(NH^4)O^6$ | 155 | | 100·00 | 100·00 |

By dry distillation the salt yields water and salicylamic acid, (Cahours):

$$C^{14}NH^9O^6 = C^{14}NH^7O^4 + 2HO.$$

When subjected to dry distillation, the salt first gives off ammonia, and is converted into an acid salt, after which the residue swells up considerably and yields hydrate of phenyl together with a sublimate of carbonate of ammonia. [? carbamic acid.] (Gerhardt.)

$$C^{14}NH^7O^6 = C^{12}H^6O^2 + NH^3,2CO^2.$$

The salt is very soluble in water.

*Salicylate of Potash.* — The acid is saturated with a concentrated solution of carbonate of potash; the liquid evaporated to dryness; the residue exhausted with strong boiling alcohol; the crystalline mass obtained from the alcoholic solution by cooling or evaporation, pressed between paper and dissolved in water; and the solution left to evaporate in vacuo. — Colourless needles having a strong silky lustre; they give off 5·05 p. c. (1 At.) water at 175°. (Cahours.)

| | *Crystallised.* | | | Cahours. |
|---|---|---|---|---|
| KO | 47·2 | | 25·48 | 25·40 |
| 14 C | 84·0 | | 45·35 | 45·12 |
| 6 H | 6·0 | | 3·25 | 3·32 |
| 6 O | 48·0 | | 25·92 | 26·16 |
| $C^{14}H^5KO^6 + Aq$ | 185·2 | | 100·00 | 100·00 |

| Or: | | | Cahours. |
|---|---|---|---|
| $C^{14}H^5KO^6$ | 176·2 | 95·14 | |
| HO | 9·0 | 4·86 | 5·05 |
| $C^{14}H^5KO^6 + Aq$ | 185·2 | 100·00 | |

The salt when dry is not altered by exposure to the air, but if moist, it soon turns brown and afterwards black. Resolved by dry distillation into hydrate of phenyl and carbonate of potash. (Cahours.) If the product of the dry distillation be saturated with hydrochloric acid and then heated with potash, an odour is produced resembling that of aniline. (Gerhardt.)

The salt dissolves readily in *alcohol* and *ether*.

*Salicylate of Baryta.* — *a. Neutral.* — When strong baryta-water is added to a boiling concentrated solution of *b*, the mixture deposits small white crystalline laminæ which may be recrystallised from a large quantity of water, apart from the air. — Small white opaque needles, concentrically grouped and having a distinct alkaline reaction. When dissolved in water, it is decomposed by carbonic acid, yielding the acid salt *b* and carbonate of baryta. At 140° in a current of dry air, it gives off 11·38 p. c. (4 At.; calc. 11·63) of water. (Piria.)

| | *Crystallised.* | | Piria. |
|---|---|---|---|
| 14 C | 84·0 | 27·13 | 27·06 |
| 8 H | 8·0 | 2·58 | 2·60 |
| 2 Ba | 137·6 | 44·44 | 44·51 |
| 10 O | 80·0 | 25·85 | 25·83 |
| $C^{14}H^4Ba^2O^6 + 2Aq$ | 309·6 | 100·00 | 100·00 |

*b. Acid.* — Obtained by boiling salicylic acid with carbonate of baryta, filtering at the boiling heat, and leaving the filtrate to evaporate in vacuo. — Short silky needles united in radiating groups. Contains 1 At. water, which is not given off at 100°, but half escapes at 150° and the rest at 218°. (Cahours.)

| | *Crystalline.* | | Cahours. |
|---|---|---|---|
| BaO | 76·6 | 35·69 | 35·56 |
| $C^{14}H^5O^6$ | 138·0 | 64·31 | |
| $C^{14}H^5BaO^6 + Aq$ | 214·6 | 100·00 | |

At a high temperature, it decomposes, giving off hydrate of phenyl and leaving carbonate of baryta mixed with charcoal. (Cahours.) — Dissolves readily in water. (Ettling.)

*Salicylate of Lime.* — *a. Neutral.* — A nearly boiling solution of lime in sugar-water containing so much sugar that it does not become turbid on boiling, is mixed with a nearly boiling solution of *b* also containing sugar, and the mixture kept for half an hour over the water-bath. — Heavy crystalline powder consisting of shining granules. Nearly insoluble in water. After drying at 100°, it contains 2 At. water of crystallisation which slowly escape (9·28 per cent.) in a stream of dry air at 180°. (Piria.)

| | | | Piria. |
|---|---|---|---|
| 14 C | 84 | 43·30 | 43·12 |
| 6 H | 6 | 3·09 | 3·15 |
| 2 Ca | 40 | 20·62 | 20·66 |
| 8 O | 64 | 32·99 | 33·07 |
| $C^{14}H^4Ca^2O^6$ + 2Aq | 194 | 100·00 | 100·00 |

Decomposed by carbonic acid like the baryta-salt. (Piria.)

*b. Acid.* — Prepared like the baryta-salt. The solution yields by evaporation in vacuo, beautiful octohedrons often of very large size. The salt has a bitter and pungent taste.

| *Crystallised.* | | | Cahours. |
|---|---|---|---|
| CaO | 28 | 16 | 16·17 |
| 14 C | 84 | 48 | 47·67 |
| 7 H | 7 | 4 | 4·03 |
| 7 O | 56 | 32 | 32·13 |
| $C^{14}H^5BaO^4$ + 2Aq | 175 | 100 | 100·00 |

Dissolves pretty readily in water. (Ettling, Cahours.)

*Salicylate of Magnesia.* — By boiling the acid with magnesia or carbonate of magnesia, and evaporating the filtrate in vacuo, the salt is obtained in radiating needles often aggregated in a compact mass. — The salt dissolves readily in cold and still more readily in boiling water. (Cahours.)

*Salicylate of Lead.* — *a. Pentabasic.* — A boiling solution of *c* is mixed with a few drops of ammonia, the liquid boiled till the precipitate becomes crystalline, and the precipitate washed with warm water and dried over quick lime. — Light powder composed of white micaceous laminæ. Has an alkaline reaction. Does not give off any water at 160°. (Piria.)

| | | | Piria. |
|---|---|---|---|
| 14 C | 84·0 | 12·39 | 12·18 |
| 4 H | 4·0 | 6·55 | 0·75 |
| 5 Pb | 517·8 | 76·39 | 76·06 |
| 9 O | 72·0 | 10·67 | 11·01 |
| $C^{14}H^4Pb^5O^6$,3PbO | 677·8 | 100·00 | 100·00 |

*b. Neutral.* — Produced by boiling *c* with water; also by dropping basic acetate of lead into a boiling solution of *c*, and then forms a heavy crystalline precipitate, which is washed with warm water and dried over quick lime. Has an alkaline reaction. Does not give off water at 100°. Decomposed by carbonic acid. (Piria.)

| | | | Piria. |
|---|---|---|---|
| 14 C | 84·0 | 24·48 | 24·37 |
| 4 H | 4·0 | 1·17 | 1·28 |
| 2 Pb | 207·6 | 60·36 | 60·41 |
| 6 O | 48·0 | 13·99 | 13·94 |
| $C^{14}H^4Pb^2O^6$ | 343·6 | 100·00 | 100·00 |

*c. Acid.* — Salicylic acid is boiled with water and carbonate of lead (avoiding an excess of the latter, according to Piria), the liquid filtered at the boiling heat, and the filtrate left to cool; or a concentrated solution of salicylate of ammonia or potash is mixed with a concentrated solution of neutral acetate of lead, the precipitate washed with cold water and dissolved in boiling water, and the solution left to cool. — Beautiful transparent crystals, which between 140° and 150° become opaque and give off 1 At. water. (Cahours.) Resolved by boiling with water into the salt *b* and free salicylic acid. (Piria.)

| | *Crystallised.* | | Cahours. |
|---|---|---|---|
| PbO | 111·8 | 44·75 | 44·59 |
| 14 C | 84·0 | 33·63 | 33·72 |
| 6 H | 6·0 | 2·40 | 2·50 |
| 6 O | 48·0 | 19·22 | 19·19 |
| $C^{14}H^5PbO^6$ + Aq.. | 249·8 | 100·00 | 100·00 |

| Or: | | | Cahours. |
|---|---|---|---|
| $C^{14}H^5PbO^6$ | 240·8 | 96·40 | |
| HO | 9·0 | 3·60 | 3·65 |
| $C^{14}H^5PbO^6$ + Aq | 249·8 | 100·00 | |

*Salicylate of Copper.* — *a. Neutral.* — Produced by heating *b* with a quantity of water not sufficient to dissolve it. Yellow-green light powder, which when heated gives off its water of crystallisation and becomes brownish, and is completely decomposed at 180°. It is sparingly soluble in boiling water, insoluble in alcohol and ether. (Piria.)

| | | | Piria. |
|---|---|---|---|
| 14 C | 84·0 | 38·63 | 38·43 |
| 6 H | 6·0 | 2·76 | 2·87 |
| 2 Cu | 63·6 | 29·18 | 28·36 |
| 8 O | 64·0 | 29·43 | 30·34 |
| $C^{14}H^4Cu^2O^6$ + 2Aq | 217·6 | 100·00 | 100·00 |

*b. Acid.* — When salicylate of baryta is decomposed by a solution of sulphate of copper, the filtrate yields long bluish green needles which may be recrystallised from water at about 60°. — The salt gives off its water of crystallisation at a temperature much below 100°, assuming at the same time a dark olive colour, and emitting vapours of salicylic acid. Above 100°, it melts and gives off copious fumes of salicylic acid. It dissolves readily in water, alcohol and ether, forming solutions of a fine yellowish green colour. When boiled with a quantity of water not sufficient to dissolve it, it is resolved into free acid and the salt *a*, being at first converted into a dark green resinous mass, which, when treated with a fresh quantity of water, becomes pulverulent and yellowish green. It is decomposed in the same manner by ether, even at ordinary temperatures. (Piria.)

| | | | Piria. |
|---|---|---|---|
| 14 C | 84·0 | 41·03 | 41·25 |
| 9 H | 9·0 | 4·40 | 4·52 |
| Cu | 31·8 | 15·50 | 15·57 |
| 10 O | 80·0 | 39·07 | 38·66 |
| $C^{14}H^5CuO^5$ + 4Aq | 204·8 | 100·00 | 100·00 |

*Salicylate of Copper and Potassium.* — Crystallised salicylic acid is added gradually and with constant agitation, to a solution of sulphate of copper and tartaric acid in excess of caustic potash, or better to a solution of tartrate of copper in moderately strong potash; the liquid then gradually acquires a green colour, and ultimately forms a green crystalline pulp, which must be dried on porous earthenware, and recrystallised from the smallest possible quantity of lukewarm water. — When slowly crystallised from the aqueous solution, it forms small rhombic tables of a beautiful emerald-green colour. It dissolves very readily in water. The deep green solution when boiled, deposits black oxide of copper and becomes colourless; a large excess of potash turns it dark blue. It does not dissolve in alcohol or ether. — In a dry stream of air, even below 100°, it gives off 14·84 p. c. (4 At.; calc. 14·82 p. c.) of water. (Piria.)

| | | | Piria. |
|---|---|---|---|
| 14 C | 84·0 | 34·57 | |
| 8 H | 8·0 | 3·29 | |
| K | 39·2 | 16·13 | 16·11 |
| Cu | 31·8 | 13·09 | 13·29 |
| 10 O | 80·0 | 32·92 | |
| $C^{14}H^4KCuO^6 + 4Aq$ | 243·0 | 100·00 | |

*Salicylate of Copper and Barium.* — The solution of the preceding salt mixed with chloride of barium, forms after awhile a light green crystalline precipitate. The salt is insoluble in water. Between 85° and 100°, it gives off 12·94 p. c. (4 At.; calc. 13·21) of water. (Piria.)

| | *At* 100°. | | Piria. |
|---|---|---|---|
| 14 C | 84·0 | 35·51 | 35·48 |
| 4 H | 4·0 | 1·69 | 1·90 |
| Ba | 68·8 | 29·09 | 28·71 |
| Cu | 31·8 | 13·41 | 13·64 |
| 6 O | 48·0 | 20·30 | 20·27 |
| $C^{14}H^4BaCuO^6$ | 236·6 | 100·00 | 100·00 |

*Salicylate of Silver.* — Nitrate of silver is precipitated by salicylate of ammonia, and the precipitate washed with cold and dissolved in boiling water (during which operations it blackens slightly: *Ettling*). As the liquid cools, the salt crystallises in transparent needles having a strong lustre. (Cahours, Ettling.) To obtain the pure salt, Ettling supersaturates salicylic acid with lime-water; passes carbonic acid through the liquid; heats it; filters; warms the filtrate and adds nitrate of silver; then washes the precipitate in the dark with cold water, and dries it at 100°.

| | | | Piria. | Delalande. | Cahours. | Ettling. |
|---|---|---|---|---|---|---|
| AgO | 116·1 | 47·37 | 46·57 | 46·80 | 46·80 | 47·68 |
| 14 C | 84·0 | 34·27 | 34·35 | 34·40 | 34·24 | 34·04 |
| 5 H | 5·0 | 2·04 | 2·09 | 2·25 | 2·11 | 2·18 |
| 5 O | 40·0 | 16·32 | 16·99 | 16·55 | 16·85 | 16·10 |
| $C^{14}H^5AgO^6$ | 245·1 | 100·00 | 100·00 | 100·00 | 100·00 | 100·00 |

The acid dissolves readily in *wood-spirit*, especially when heated, readily in *alcohol*, and abundantly in *ether*, especially when heated. It is nearly insoluble in cold *oil of turpentine*, but dissolves in 5 pts. of that liquid at the boiling heat, and solidifies on cooling. (Cahours.)

For Salicylate of Methyl, see page 258.

## Methylsalicylic Acid.

$C^{16}H^8O^6 = C^2H^3O,C^{14}H^5O^5$.

CAHOURS. (1843.) *Compt. rend.* 16, 853; *N. J. Pharm.* 3, 364. — *N. Ann. Chim. Phys.* 10, 327; 27, 5. — *Compt. rend.* 39, 255; *Pharm. Centr.* 1843, 698; 1844, 434; 1854, 658.

PROCTER. *N. J. Pharm.* 3, 275; *J. pr. Chem.* 29, 467; *Ann. Pharm.* 48, 66; *Pharm. Centr.* 1843, 699.

GERHARDT. *Compt. rend.* 38, 32; *Ann. Pharm.* 89, 362; *J. pr. Chem.* 61, 89; *Traité*, 3, 827; *Pharm. Centr.* 1854, 129.

*Gaultheriasäure, Methylspiroylsäure, Hydrated Methyl-salicyl, Salicylformester.*

Occurs in the herb of *Gaultheria procumbens* (New Jersey), forming $\frac{9}{10}$ of the volatile oil (wintergreen-oil) obtained therefrom by distillation with water. (Cahours.)

*Preparation.* 1. The volatile oil obtained by distilling the herb of *Gaultheria procumbens* with water,—or the commercial oil of wintergreen,—is rectified, and the portion which distils over at 222° collected apart. The oil begins to boil at 200°, the boiling point quickly rising to 222°; The portion which first distils over contains a light oil having the composition of oil of turpentine. (Procter, Cahours.) — 2. Two pts. of crystallised salicylic acid are distilled with 2 pts. of anhydrous methylic alcohol and 1 pt. of oil of vitriol. (Cahours.) — 3. Absolute methylic alcohol is gradually added to chloride of salicyl; and, as soon as the first action, which is accompanied with great rise of temperature and evolution of hydrochloric acid, has ceased, the product is distilled, and the portion which goes over at 222°, collected. (Gerhardt.)

*Properties.* Colourless oil. Commercial wintergreen-oil is reddish yellow; but may be rendered yellowish or even colourless by rectification. (Procter.) — Has an agreeable, very penetrating odour, and a sweet, cooling, aromatic taste. Sp. gr. 1·18 at 10°. Boils constantly at 222°. Vapour-density 5·42. (Cahours.)

| | | | | Cahours. a. | Cahours. b. |
|---|---|---|---|---|---|
| 16 C | 96 | 63·15 | | 63·13 | 63·03 |
| 8 H | 8 | 5·26 | | 5·43 | 5·37 |
| 6 O | 48 | 31·59 | | 31·44 | 31·60 |
| $C^{16}H^8O^6$ | 152 | 100·00 | | 100·00 | 100·00 |

| | Vol. | Density. |
|---|---|---|
| C-vapour | 16 | 6·6560 |
| H-gas | 8 | 0·5544 |
| O-gas | 3 | 3·3279 |
| Vapour of Methylsalicylic acid ... | 2 | 10·5383 |
| | 1 | 5·7191 |

*a* was prepared by (1); *b*, by (2).—The compound is isomeric with anisic acid.

*Decompositions.* When the acid is mixed with strong *nitric acid*, violent spirting takes place, if the mixture is not cooled, but when it is kept cool, methylnitrosalicylic acid is produced. (Cahours.) By fuming nitric acid, it is converted into methylnitrosalicylic acid; by a mixture of fuming nitric acid and oil of vitriol, into methylbinitrosalicylic acid, or by longer action, into methylternitrosalicylic acid. (Cahours.) — 2. *Bromine* added by drops to methylsalicylic acid, causes considerable rise of temperature and evolution of hydrobromic acid; the mass which solidifies on cooling contains methylbromosalicylic and methylbibromosalicylic acids; the proportions varying according to the quantity of bromine used. *Chlorine* forms similar products, the quantity of hydrogen replaced never exceeding 2 At. even in sunshine. (Procter, Cahours.) — 3. *Pentachloride of phosphorus* acts violently on the acid, forming chloride of salicyl, chloride of methyl and chlorophosphoric acid.

$$C^{16}H^8O^6 + PCl^5 = C^{14}ClH^5O^4 + C^2H^3Cl + PCl^3O^2.$$

Gerhardt (*Traité*, 9, 343) supposes that phosphate of salicyl is formed in this reaction:

$$4C^{16}H^8O^6 + PCl^5 = 4C^2H^3Cl + C^{14}ClH^5O^4 + P(C^{14}H^5O^4)^3O^8,$$

thereby explaining why so small a quantity of chlorophosphoric acid is formed, and why, after treating the resulting chloride of salicyl with alcohol, and distilling off the salicylate of ethyl thereby produced, a considerable residue is left. — 4. *Chloride of succinyl, chloride of benzoyl* and *chloride of cumyl* form with methylsalicylic acid: methylsalicyl-succinate, — benzoate and — cuminate, together with hydrochloric acid: *e. g.*:

$$C^{14}(C^2H^3)H^5O^6 + C^{14}H^5ClO^2 = C^{14}(C^2H^5)(C^{14}H^5O^2)H^4O^6 + HCl \text{ (Gerhardt).}$$

5. By *potash-ley*, methylsalicylic acid is resolved, after a few hours at ordinary temperatures, immediately when heated, into salicylic acid and wood-spirit. (Procter, Cahours.) — Heated with anhydrous baryta, it yields carbonate of baryta and anisol. — 7. With *ammonia*, either gaseous or alcoholic, it forms salicylamide [salicylamic acid] and wood spirit:

$$C^{16}H^8O^6 + NH^3 = C^{14}NH^7O^4 + C^2H^4O^2.$$

8. When pieces of potassium are dropped into methylsalicylic acid heated to between 30° and 60°, the temperature rises, gas is evolved, and after the addition of a considerable quantity of potassium, the mass solidifies, even if kept at 105°. Soon afterwards it takes fire and leaves a black residue. In one experiment, salicylous acid was produced. (Cahours.)

*Combinations.* The acid dissolves sparingly in *water*, imparting however its taste and smell; the solution is coloured violet by ferric salts.

It dissolves *iodine* without decomposition, forming a brown solution.

Methylsalicylic acid unites with *bases*, forming salts in which 1 At. hydrogen is replaced by a metal. Before Piria had demonstrated the bibasic character of salicylic acid, Gerhardt supposed that salicylate of methyl, and the other compound ethers of salicylic acid, should be regarded as salicylic acid in which 1 At. hydrogen is replaced by an alcohol-radical ($C^2H^3$, $C^4H^5$ . . .), but that the hydrogen-atom thus replaced was different from that which in the salicylates is replaced by a metal (or in the compound ethers of other acids by an alcohol-radical), and consequently that the place of the latter might still be taken by a metal (or by an acid radical). Thus, the formula of salicylic acid (supposed monobasic) being $\left.\begin{matrix}C^{14}H^5O^4\\H\end{matrix}\right\}O^2$, that of methylsalicylic acid would be $\left.\begin{matrix}C^{14}H^4(C^2H^3)O^4\\H\end{matrix}\right\}O^2$, and of its potash-salt, $\left.\begin{matrix}C^{14}H^4(C^4H^3)O^4\\K\end{matrix}\right\}O^2$

*Methylsalicylate of Potash.* — With strong potash-ley, methylsalicylic acid forms a mass which solidifies in the crystalline form. When potash-ley of 45° Bm. free from carbonic acid and diluted with an equal bulk of water, is shaken up with excess of methylsalicylic acid, the potash-salt separates in pearly scales, which must be washed with the smallest possible quantity of cold water, pressed between bibulous paper, and dissolved in absolute alcohol, a small quantity of carbonate of potash then remaining undissolved; the solution is left to evaporate in vacuo. — Extremely delicate, white needles having a strong lustre and resembling asbestos. (Cahours.) Six-sided tables. (Procter.)

| | | | | Cahours. |
|---|---|---|---|---|
| KO | 47·2 | 24·82 | | 24·95 |
| 16 C | 96·0 | 50·47 | | 49·07 |
| 7 H | 7·0 | 3·68 | | 3·77 |
| 5 O | 40·0 | 21·03 | | 22·21 |
| $C^{16}H^7KO^6$ | 190·2 | 100·00 | | 100·00 |

According to Cahours, the compound still contains water, which cannot be separated, and appears to be $C^{16}H^7KO^6 + \frac{1}{2}Aq$, that formula requiring 24·24 p. c. KO, 49·31 p. c. C and 3·85 p. c. H.

It dissolves abundantly in *water*.

When heated in the moist state, it is converted into salicylate of potash. (Cahours.) The solution colours ferric salts purple. (Procter.)

It dissolves very easily in *alcohol* and *ether*. (Procter.)

*Methylsalicylate of Soda.* — Resembles the potash-salt, but is less soluble in water, alcohol and ether. (Cahours, Procter.)

*Methylsalicylate of Baryta.* — When methylsalicylic acid is added by drops to hot baryta-water, crystalline flocks separate out, which increase in quantity as the liquid cools, and at last, white crystalline scales are formed. These are washed on the filter, first with water, then with alcohol, and dried in vacuo.

| | | | | Cahours. |
|---|---|---|---|---|
| BaO | 76·6 | 33·51 | | 34·47 |
| 16 C | 96·0 | 41·99 | | 41·98 |
| 8 H | 8·0 | 3·50 | | 3·45 |
| 6 O | 48·0 | 21·00 | | 20·10 |
| $C^{16}H^7BaO^6 + Aq$ | 228·6 | 100·00 | | 100·00 |

By dry distillation it is completely resolved into carbonate of baryta, anisol, and free carbonic acid:

$$C^{16}H^6BaO^5 + 2HO = C^{14}H^8O^2 + BaO,CO^2 + CO^2.$$

This decomposition tends to support the formula given by Cahours, whereas the baryta-determination seems to show that the salt is anhydrous (calculated quantity of BaO=34·88 p. c.). [Perhaps the salt analysed contained carbonate of baryta. L.]

The potash-salt forms precipitates with the salts of lead, copper, silver and mercury. (Procter, Cahours.)

*Compounds in which the Basic Hydrogen of Methylsalicylic acid is replaced by Methyl, Ethyl or Amyl,* are obtained by heating methylsalicylate of potash with iodide of methyl, ethyl or amyl in sealed tubes. The methyl-compound (salicylate of methyl, $2C^2H^3O,C^{14}H^4O^4$) boils at 248°; the ethyl-compound ($=C^8H^3O,C^4H^5O,C^{14}H^4O^4$) at 262°, and the amyl-compound at a temperature above 300°. They may be obtained in the crystalline form. (Cahours, *Compt. rend.* 39, 256.)

Methylsalicylic acid mixes in all proportions with alcohol, ether, oil of turpentine and oil of lemons.

*Succinate of Methylsalicyl.* $C^{40}H^{18}O^{16} = 2C^{16}H^7O^5,C^8H^4O^6 = C^8H^4(C^{16}H^7O^5)^2O^6$. — Prepared by gently heating chloride of succinyl (x, 136) with about 2 pts. of methylsalicylic acid as long as hydrochloric acid continues to escape, digesting the resulting brown mass with potash-ley, and crystallising it from boiling alcohol. The solution on cooling deposits large rectangular laminæ composed of easily separated fibres. The compound is sparingly soluble in ether. (Gerhardt.) According to Gerhardt, it is to be regarded as 2 At. salicylic acid in which 2 At. hydrogen are replaced by methyl and other 2 At. hydrogen by 1 At. succinyl: $C^{28}H^8(C^2H^3)^2(C^8H^4O^4)O^{12}$.

*Benzoate of Methylsalicyl.* $C^{30}H^{12}O^8=C^{16}H^7O^5,C^{14}H^5O^3$, according to Gerhardt $C^{14}(C^2H^3)(C^{14}H^5O^3)H^4O^6$. — Obtained by heating equal parts of salicylate of methyl and chloride of benzoyl, as long as hydrochloric acid continues to escape, washing the tenacious, gradually crystallising product with potash-ley, and crystallising from alcohol or ether. — Oblique rhombic prisms having a splendid lustre. They remain unaltered in warm water. When heated with caustic potash, they are strongly attacked, and give off an aromatic odour; and on treating the aqueous solution of the residue with hydrochloric acid, a precipitate of salicylic acid is obtained. The compound is insoluble in water, but dissolves readily in alcohol and ether. (Gerhardt.)

## Ethylsalicylic Acid.

$C^{18}H^{10}O^6 = C^4H^5O,C^{14}H^5O^5$.

CAHOURS. (1844.) *N. Ann. Chim. Phys.* 10, 360.—*Compt. rend.* 28, 586; *J. pr. Chem.* 47, 417.—*N. Ann. Chim. Phys.* 27, 463; *Ann. Pharm.* 74, 314; *J. pr. Chem.* 49, 283; *Compt. rend.* 39, 256.

G. BALY. *Chem. Soc. Qu. J.* 2, 28; *Ann. Pharm.* 70, 269.—*J. pr. Chem.* 47, 419; *Pharm. Centr.* 1849, 715.

GERHARDT. *Compt. rend.* 38, 32; *Ann. Pharm.* 89, 362; *J. pr. Chem.* 61, 89; *Pharm. Centr.* 1854, 129.—*Traité*, 3, 326.

***Salicylate of ethyl, Salicylic ether, Salicylvinester.***

*Preparation.* When 4 pts. of alcohol are distilled with 3 pts. of crystallised salicylic acid and 2 pts. of oil of vitriol, alcohol alone passes over first, then a mixture of alcohol and salicylic ether, and lastly a small quantity of alcohol with a large quantity of salicylic ether. As soon as sulphurous acid begins to escape, the distillation is interrupted, the distillate shaken up with water containing a little ammonia, then washed with water, dried over chloride of calcium, and rectified by two distillations. (Cahours, Baly.) — 2. When absolute alcohol is added by drops to chloride of salicyl, the mixture becomes heated and gives off large quantities of hydrochloric acid. As soon as the action ceases, the liquid is distilled, and the portion which goes over towards 225° is collected. (Gerhardt.)

*Properties.* Colourless oil heavier than water. (Cahours.) Sp. gr. 1·097 (Baly); 1·1843 at 10° (Delffs). Boils at 225° (Cahours), at 221° with the barometer at 28″ 1·3‴ (Delffs); at 229·5°. (Baly.) It has an agreeable odour, resembling that of salicylate of methyl. (Cahours.)

| | | | Cahours. |
|---|---|---|---|
| 18 C | 108 | 65·06 | 64·78 |
| 10 H | 10 | 6·03 | 6·10 |
| 6 O | 48 | 28·91 | 29·12 |
| $C^{18}H^{10}O^6$ | 166 | 100·00 | 100·00 |

*Decompositions.* 1. The compound is rapidly attacked by *chlorine* and *bromine*, with formation of substitution-products. (Cahours.) — 2. When fuming *nitric acid* is added to it by drops, it becomes heated, turns red and dissolves; on addition of water, ethylnitrosalicylic acid is precipitated in the form of an oil, which after a while solidifies in a yellowish mass. When ethylsalicylic acid is heated with excess of nitric acid, picric acid is produced. (Cahours.) — 3. Heated with aqueous *alkalis*, it is resolved into salicylic acid and alcohol. — 4. When brought in contact with anhydrous baryta, it becomes hot, and yields phenetol by distillation. (Baly, Cahours.)—5. Placed together with caustic ammonia in a closed vessel, it disappears after a while, and a brown liquid is formed containing alcohol and salicylamide. (Cahours.) — 6. Pentachlo-

ride of phosphorus and chloride of benzoyl act on ethylsalicylic in the same manner as on methylsalicylic acid. (Gerhardt.)

*Combinations.* With bases, the acid forms compounds similar to those of methylsalicylic acid. The potassium and sodium-compounds are crystallisable, soluble in water, and exactly similar to the corresponding salts of methylsalicylic acid. Baryta forms a crystalline compound sparingly soluble in water. (Cahours.)

By heating ethylsalicylic acid with iodide of methyl, ethyl or amyl in a sealed tube, compounds are obtained in which the basic atom of hydrogen (that which might be replaced by a metal) is replaced by methyl, ethyl, or amyl.

*Benzoate of Ethyl-salicyl.* $C^{32}H^{14}O^8 = C^{18}H^9O^5,C^{14}H^5O^3$, or, according to Gerhardt, $C^{14}H^4(C^4H^5)C^{14}H^5O^2)O^6$. Prepared by heating ethylsalicylic acid with chloride of benzoyl, as long as hydrochloric acid continues to escape. The mass which crystallises on cooling separates from the ethereal solution by spontaneous evaporation in the form of an oil, which gradually solidifies, by the separation of crystalline nodules consisting of small needles. Dissolves readily in alcohol and ether. (Gerhardt.)

## Amylsalicylic Acid.

$C^{24}H^{16}O^6 = C^{10}H^{11}O,C^{14}H^5O^5$.

DRION. *Compt. rend.* 38, 123; *Ann. Pharm.* 92, 513; *J. pr. Chem.* 62, 480.

*Formation.* Only by the action of chloride of salicyl on fusel-oil. (Drion, *comp.* Schlieper, *Ann. Pharm.* 59, 26.)

*Preparation.* By means of chloride of salicyl, in the same manner as methylsalicylic and ethylsalicylic acids. It is necessary to operate with small quantities only; otherwise the action becomes too violent, and a large quantity of carbolic acid is produced. (Drion.)

*Properties.* Colourless, strongly refracting liquid, heavier than water, boiling at 270°, and having an agreeable odour.

Boiled with potash, it yields amylic alcohol, and salicylate of potash.

It is insoluble in water. With cold potash-ley, it forms amylsalicylate of potash. (Drion.)

Heated with chloride of benzoyl, it gives off hydrochloric acid, and yields a body which crystallises in needles (benzoate of amylsalicyl?) (Gerhardt); a viscid mass which does not readily solidify. (Drion.)

*Derivatives of the Acid Salicylic Ethers, which may be regarded as belonging to the Benzene-series.*

## Anisol.

$C^{14}H^8O^2 = C^2H^3O,C^{12}H^5O.$

CAHOURS. (1841.) *N. Ann. Chim. Phys.* 2, 296; *Ann. Pharm.* 41, 69; *J. pr. Chem.* 24, 352; *Pharm. Centr.* 1841, 682.—*Compt. rend.* 15, 804.—*N. Ann. Chim. Phys.* 10, 354; 27, 440; *Ann. Pharm.* 74, 298; *Pharm. Centr.* 1844, 435.—*Compt. rend.* 32, 60; *Ann. Pharm.* 78, 125.

LAURENT. *Rev. scient.* 11, 258; *Compt. rend.* 15, 953.

*Dracol, Phenate de methyle, Carbolate of methyl* [*Carbolformester*].

*Formation and Preparation.* 1. Carbolate of potash and iodide of methyl are heated together in a sealed tube to a temperature between 100° and 120°. Decomposition takes place quickly, according to the following equation:

$$C^{12}H^5KO^2 + C^2H^3I = C^2H^3O,C^{12}H^5O + KI.$$

Or carbolate of potash is distilled with methylosulphate of potash.—2. Methysalicylate of baryta is subjected to dry distillation (p. 258). Or salicylate of methyl is slowly dropped upon a very large excess of finely pulverised anhydrous baryta, whereupon considerable rise of temperature takes place; the mixture is distilled; and the oil which passes over, is repeatedly washed with water containing potash, then dried over chloride of calcium and rectified.—3. Anisic acid is distilled with excess of baryta:

$$C^{16}H^8O^6 = C^{14}H^8O^2 + 2CO^2.$$

*Properties.* Colourless, transparent, very thin liquid having an agreeable aromatic taste. Sp. gr. 0·991 at 15°. Boils at 152°.

| | | | Cahours. |
|---|---|---|---|
| 14 C | 84 | 77·77 | 77·58 |
| 8 H | 8 | 7·40 | 7·59 |
| 2 O | 16 | 14·83 | 14·83 |
| $C^{14}H^8O^2$ | 108 | 100·00 | 100·00 |

Isomeric with benzylic alcohol.

*Decompositions.* 1. Anisol is rapidly attacked by fuming *nitric acid*, and if the liquid be well cooled, nitranisol is produced, but by boiling for a little while, binitranisol is obtained. Treated with nitrosulphuric acid, it yields ternitranisol. (Cahours, Laurent.) Chrysanisic acid is also frequently obtained. (Cahours.)—2. With *bromine*, anisol forms two crystalline products, bromanisol, $C^{14}BrH^7O^2$, and bibromanisol, the former of which is difficult to purify. *Chlorine* acts in a similar manner.—3. With *oil of vitriol*, anisol yields sulphanisolic acid. In fuming sulphuric acid it dissolves with evolution of heat, forming a bright red

solution, from which water throws down sulphanisolide, whilst sulphanisolic acid remains dissolved; with the vapour of fuming sulphuric acid also, the products formed are sulphanisolide and sulphanisolic acid.

Anisol is not altered by distillation over anhydrous phosphoric acid.

It is insoluble in water, but dissolves in *alcohol* and *ether*.

## Sulphanisolide.

$C^{14}H^7SO^4 = C^{14}H^7(SO^2)O^2$.

CAHOURS. (1844.) *N. Ann. Chim. Phys.* 10, 354; 27, 460; *Ann. Pharm.* 74, 31; *J. pr. Chem.* 49, 280.

*Formation.* By the action of anhydrous sulphuric acid on anisol.

*Preparation.* When vapour of anhydrous sulphuric acid is passed over anisol which is kept cool, and the thickened liquid is mixed with water, unaltered anisol separates out, together with a solid mass, while sulphanisolic acid dissolves. The anisol is removed, the solid mass collected on a filter, washed, dried, and dissolved in alcohol, and the solution left to evaporate.

*Properties.* Delicate needles having a silvery lustre. Melts when carefully heated and solidifies at a higher temperature.

| | | | Cahours. |
|---|---|---|---|
| 14 C | 84 | 60·43 | 60·23 |
| 7 H | 7 | 5·03 | 5·16 |
| S | 16 | 11·51 | |
| 4 O | 32 | 23·03 | |
| $C^{14}H^7SO^4$ | 139 | 100·00 | |

The compound dissolves in oil of vitriol, forming sulphanisolic acid.

It is insoluble in water, but dissolves readily in *alcohol* and *ether*, separating therefrom in prisms as the solution evaporates.

*Sulphanisolic acid* is soluble in water and crystallises in needles. — Its salts are also soluble in water. The baryta-salt crystallises in white scales having a strong lustre, and has when dry, the composition $C^{14}H^8O^2,BaO,2SO^3$. (Cahours.)

## Bromanisol.

$C^{14}BrH^7O^2 = C^2H^3O,C^{12}BrH^4O$.

CAHOURS. (1844.) *N. Ann. Chim. Phys.* 10, 356; 14, 496.—*Ann. Pharm.* 52, 330.

*Anisole monobromé, Bromcarbolformester.*

Formed by treating anisol with bromine, but cannot by this process be obtained sufficiently pure. Passes over in the form of an oil when bromanisate of potash is distilled by itself or when bromanisic acid is distilled with baryta.

| | | | | | Cahours. |
|---|---|---|---|---|---|
| 14 C | 84 | | 48·73 | | 49·16 |
| 7 H | 7 | | 3·55 | | 3·69 |
| Br | 80 | | 39·59 | | 39·15 |
| 2 O | 16 | | 8·13 | | 8·00 |
| $C^{14}H^7BrO^2$ | 187 | | 100·00 | | 100·00 |

## Bibromanisol.

$C^{14}Br^2H^6O^2 = C^2H^3O,C^{14}Br^2H^3O.$

CAHOURS. (1844.) *N. Ann. Chim. Phys.* 10, 356; *Ann. Pharm.* 52, 330.

*Anisole bibromé, Bibromcarbolformester.*

Produced, simultaneously with bromanisol, by the action of bromine upon anisol, and crystallises on cooling from its solution in boiling alcohol in crystalline laminæ having a strong lustre. Melts at 54°. Volatilises without residue, and is deposited on the colder part of the retort in well defined tables having a strong lustre.

| | | | | | Cahours. |
|---|---|---|---|---|---|
| 14 C | 84 | | 31·58 | | 31·73 |
| 6 H | 6 | | 2·26 | | 2·34 |
| 2 Br | 160 | | 60·15 | | 59·93 |
| 2 O | 16 | | 6·01 | | 6·00 |
| $C^{14}Br^2H^6O^2$ | 266 | | 100·00 | | 100·00 |

## Nitranisol.

$C^{14}NH^7O^6 = C^2H^3O,C^{12}XH^4O.$

CAHOURS. (1849.) *Compt. rend.* 28, 381.—*N. Ann. Chim. Phys.* 27, 441; *Ann. Pharm.* 74, 299; *J. pr. Chem.* 49, 263; *Pharm. Centr.* 1849, 308.

*Anisole mononitrique, Nitrocarbolformester.*

*Formation and Preparation.* When fuming nitric acid is gradually added to anisol well and constantly cooled, a thick, oily, black-blue liquid is produced; and on repeatedly washing this liquid with alkaline water, then dehydrating it with chloride of calcium and distilling, unaltered anisol passes over at first, and the receiver must be changed as soon as the boiling point reaches 260°.

*Properties.* Amber-coloured oil, heavier than water. Boils between 262° and 264°. Has an aromatic odour somewhat like that of bitter almonds.

| | | | Cahours. |
|---|---|---|---|
| 14 C | 84 | 54·91 | 55·19 |
| N | 14 | 9·15 | 9·29 |
| 7 H | 7 | 4·57 | 4·84 |
| 6 O | 48 | 31·37 | 30·68 |
| $C^{14}NH^7O^6$ | 153 | 100·00 | 100·00 |

Heated with fuming nitric acid, it is converted, first into binitranisol and afterwards into ternitranisol. — It is quickly decomposed by alcoholic hydrosulphate of ammonia, sulphur being separated and anisidine produced :

$$C^{14}NH^7O^6 + 6HS = C^{14}NH^9O^2 + 4HO + 6S.$$

It is not decomposed by alcoholic potash, even at high temperatures.

Dissolves in oil of vitriol and is separated therefrom in its original state by water.

## Binitranisol.

$$C^{14}N^2H^6O^{10} = C^2H^3O,C^{12}X^2H^3O.$$

CAHOURS. (1844.) *N. Ann. Chim. Phys.* 10, 356. — *Compt. rend.* 27, 486; *N. Ann. Chim. Phys.* 25, 21; *J. pr. Chem.* 46, 333; *Ann. Pharm.* 69, 236. — *N. Ann. Chim. Phys.* 27, 441; *Ann. Pharm.* 74, 299; *J. pr. Chem.* 49, 263; *Pharm. Centr.* 1844, 436 ; 1849, 165, 308.

***Anisole binitrique, Binitrocarbolformester.***

*Formation.* 1. By boiling anisol for a short time with fuming nitric acid. — 2. By boiling anisic acid for a longer time with fuming nitric acid :

$$C^8H^5O^6 + 2NO^5 = C^{14}N^2H^6O^{10} + 2CO^2 + 2HO.$$

*Preparation.* 1. When anisol is boiled for a few minutes with fuming nitric acid, and the liquid mixed with water, a heavy oil separates out, which solidifies in a buttery mass, forming with boiling alcohol a splendid chrome-green solution, which, when perfectly cold, yields colourless needles. — 2. When a solution of anisic acid in nitrosulphuric acid is boiled for an hour, carbonic acid is evolved, and a mixture of picric acid and binitranisol is obtained [by precipitation with water? Gm.], from which the picric acid may be extracted by potash.

*Properties.* Long pale yellow needles. Melts at 85° or 86°, and sublimes at a higher temperature in slender needles.

| | | | Cahours. | |
|---|---|---|---|---|
| | | | *a.* | *b.* |
| 14 C | 84 | 42·35 | 42·26 | 42·20 |
| 2 N | 28 | 14·14 | 14·21 | 14·24 |
| 6 H | 6 | 3·02 | 3·16 | 3·02 |
| 10 O | 80 | 40·49 | 40·37 | 40·54 |
| $C^{14}N^2H^6O^{10}$ | 198 | 100·00 | 100·00 | 100·00 |

*a* was prepared from anisol, *b* from anisic acid.

It is decomposed by strong potash, but only after continued boiling.

By alcoholic potash it is quickly resolved into binitrocarbolic acid and wood-spirit.

With hydrosulphate of ammonia it yields nitranisidine.

It is insoluble in water, but dissolves in boiling *alcohol*, forming a solution of a splendid chrome-green colour.

## Ternitranisol.

CAHOURS. (1848.) *Compt. rend.* 27, 486.—*N. Ann. Chim. Phys.* 25, 23; *Ann. Pharm.* 69, 238; *J. pr. Chem.* 46, 336.—*N. Ann. Chim. Phys.* 27, 441; *Ann. Pharm.* 74, 299; *J. pr. Chem.* 49, 263; *Pharm. Centr.* 1849, 165, 308.

*Formation and Preparation.* 1. By treating anisol with fuming nitrosulphuric acid.—2. When the colourless solution of 1 pt. of anisic acid in 15 pts. of a mixture of equal pts. of fuming nitric acid and fuming oil of vitriol, is gently heated till it becomes turbid, two layers are formed, one of which is oily and solidifies on cooling. The acid liquid diluted with a large quantity of water, immediately yields a heavy oil which on cooling solidifies in a pale yellow mass. This mass is freed from all acids by boiling, then dissolved in a mixture of ether and alcohol, and the solution is left to evaporate.

*Properties.* Tabular crystals having a very pale yellow colour and strong lustre. From a solution in anhydrous ether, the compound crystallises by very slow evaporation in rhomboidal tables having a scarcely perceptible yellow colour. It melts between 58° and 60°. When gradually heated, it sublimes undecomposed.

| | | | Cahours. |
|---|---|---|---|
| 14 C | 84 | 34·56 | 34·43 |
| 3 N | 42 | 17·28 | 17·29 |
| 5 H | 5 | 2·05 | 2·29 |
| 14 O | 112 | 46·11 | 45·99 |
| $C^{14}N^{3}H^{5}O^{14}$ | 263 | 100·00 | 100·00 |

*Decompositions.* The compound is not altered by boiling with aqueous ammonia or dilute potash-ley. When boiled with moderately strong potash-ley, it yields picrate of potash and wood-spirit. When it is treated with hydrosulphate of ammonia, sulphur is separated and binitranisidine produced.

It does not dissolve in water, even at the boiling heat. It dissolves without decomposition in oil of vitriol and hot nitric acid.

It dissolves pretty readily in *alcohol*, whence it separates for the most part on cooling, more readily in a mixture of equal parts of alcohol and ether, easily in *ether*.

## Anisidine.

$C^{14}NH^{9}O^{2} = C^{14}AdH^{5}O^{2},H^{2}$ ?

CAHOURS. (1849.) *Compt. rend.* 28, 382.—*N. Ann. Chim. Phys.* 27, 445; *Ann. Pharm.* 74, 300; *J. pr. Chem.* 49, 265.—*Pharm. Centr.* 1849, 308.

*Formation.* (p. 264).

*Preparation.* When nitranisol is dissolved in alcoholic hydrosulphate of ammonia, and the solution is evaporated down to between ⅓ and ¼, then mixed with hydrochloric acid and a small quantity of water, and filtered from the separated sulphur, the filtrate yields by evaporation, needles of hydrochlorate of anisidine, which, when distilled with strong potash-ley, yield an oil which crystallises on cooling.

| | | | Cahours. |
|---|---|---|---|
| 14 C | 84 | 68·29 | 67·85 |
| N | 14 | 11·3 | |
| 9 H | 9 | 7·32 | 7·15 |
| 2 O | 16 | 13·01 | |
| $C^{14}NH^{9}O^{2}$ | 121 | 100·00 | |

With hydrochloric acid, anisidine forms a salt which crystallises in slender needles. It also forms crystallisable salts with sulphuric and nitric acid.

*Chloroplatinate of Anisidine* is formed on mixing the hydrochlorate with a hot concentrated solution of bichloride of platinum, and separates in yellow needles on cooling.

The oxalate is a crystallisable salt.

## Nitranisidine.

$C^{14}N^{2}H^{8}O^{6} = C^{14}AdXH^{4}O^{2},H^{2}$.

CAHOURS. (1849.) *Compt. rend.* 28, 383.—*N. Ann. Chim. Phys.* 27, 445; *Ann. Pharm.* 74, 301; *J. pr. Chem.* 49, 266.—*Pharm. Centr.* 1849, 308.

*Anisidine nitrique.*

*Formation.* (p. 265).

*Preparation.* An alcoholic solution of bi-hydrosulphate of ammonia is added to an alcoholic solution of binitranisol; the liquid evaporated to one-third at a gentle heat, then supersaturated with hydrochloric acid, heated to the boiling point, filtered from the separated sulphur, and precipitated by excess of ammonia; the reddish crystalline precipitate is washed with water, dried, and dissolved in boiling alcohol; and the solution left to cool slowly.

*Properties.* Garnet-red needles having a strong lustre. Melts when heated and crystallises on cooling in a mass consisting of needles arranged in radiated groups. When carefully heated above the melting point, it forms vapours which condense in yellow needles.

| | | | | Cahours. |
|---|---|---|---|---|
| 14 C | 84 | 50·09 | | 49·99 |
| 2 N | 28 | 16·67 | | 16·56 |
| 8 H | 8 | 4·67 | | 4·85 |
| 6 O | 48 | 28·57 | | 28·60 |
| $C^{14}N^2H^8O^6$ | 168 | 100·00 | | 100·00 |

Bromine acts violently on nitranisidine, forming a resinous mass, which does not exhibit basic properties. — With slightly heated fuming nitric acid, it evolves a large quantity of red vapours, and forms a gummy mass insoluble in acids and turning brown-red in contact with alkalies.

Nitranisidine is not altered by chloride of benzoyl at ordinary temperatures; but on gradually heating the mass, a violent action takes place, hydrochloric acid being evolved and benzonitranisidide produced:

$$C^{14}N^2H^8O^6 + C^{14}H^5ClO^2 = C^{28}N^3H^{12}O^8 + ClH.$$

It is insoluble in cold water, but dissolves in hot *water* so abundantly that the solution solidifies on cooling.

The *salts of nitranisidine* are colourless when pure.

*Sulphate of Nitranisidine.* — When nitranisidine is dissolved in gently heated oil of vitriol diluted with a treble quantity of water (the solution of the crude base is black-brown, that of the purified base nearly colourless), the solution, after evaporation over the water-bath, yields on cooling a dark-brown crystalline mass, which becomes nearly colourless when pressed between paper. It is recrystallised in vacuo. — Slender, colourless, silky needles united in radiated groups.

It dissolves readily in water, especially if acidulated with sulphuric acid.

| | | | | Cahours. |
|---|---|---|---|---|
| 14 C | 84 | 38·71 | | 38·77 |
| 2 N | 28 | 12·90 | | 12·63 |
| 9 H | 9 | 4·14 | | 4·26 |
| 7 O | 56 | 25·80 | | |
| $SO^3$ | 40 | 18·45 | | |
| $C^{14}N^2H^8O^6,SO^4H$ | 217 | 100·00 | | |

*Hydrobromate of Nitranisidine.* — Obtained by dissolving nitranisidine in the boiling aqueous acid. After purification it forms colourless needles $= C^{14}N^2H^8O^6,HBr$.

*Hydrochlorate of Nitranisidine.* — The solution of nitranisidine in boiling hydrochloric acid yields on cooling brownish needles, which become colourless when pressed between paper and several times recrystallised. They dissolve with great facility in boiling water.

| | | | Cahours. |
|---|---|---|---|
| 14 C | 84·0 | 41·07 | 40·89 |
| 2 N | 28·0 | 13·69 | 13·56 |
| 9 H | 9·0 | 4·40 | 4·47 |
| 6 O | 48·0 | 23·48 | 23·52 |
| Cl | 35·5 | 17·36 | 17·56 |
| $C^{14}N^{2}H^{8}O^{6},ClH$ | 204·5 | 100·00 | 100·00 |

*Nitrate of Nitranisidine.* — When nitric acid of sp. gr. 1·36 diluted with an equal bulk of water, is saturated while hot with nitranisidine, the salt crystallises out almost completely on cooling in brown needles, which must be pressed between paper, dissolved to saturation in boiling water containing a few drops of nitric acid, and the solution slowly evaporated. — Large needles easily soluble in hot water, nearly insoluble in cold water.

| | | | Cahours. |
|---|---|---|---|
| 14 C | 84 | 36·37 | 36·43 |
| 3 N | 42 | 18·19 | 18·05 |
| 9 H | 9 | 3·89 | 2·82 |
| 12 O | 96 | 41·55 | 42·70 |
| $C^{14}N^{2}H^{8}O^{6},NO^{6}H$ | 231 | 100·00 | 100·00 |

*Chloroplatinate of Nitranisidine.* — Obtained by mixing the hot concentrated solutions of bichloride of platinum and hydrochlorate of nitranisidine. Crystallises on cooling in brownish orange-coloured needles.

| | | | Cahours. |
|---|---|---|---|
| 14 C | 84·0 | 22·45 | 22·34 |
| 2 N | 28·0 | 7·48 | |
| 9 H | 9·0 | 2·41 | 2·61 |
| 6 O | 48·0 | 12·86 | |
| Pt | 98·7 | 26·34 | 26·25 |
| 3 Cl | 106·5 | 28·46 | |
| $C^{14}N^{2}H^{8}O^{6},HCl,PtCl^{2}$ | 374·2 | 100·00 | |

Nitranisidine dissolves abundantly in boiling *alcohol*, the greater par crystallising out again on cooling.

It dissolves readily in *ether*, especially when warm, and crystallises therefrom in long orange-yellow needles.

## Binitranisidine.

$C^{14}N^{3}H^{7}O^{10} = C^{14}AdX^{2}H^{3}O^{2},H^{2}$.

CAHOURS. *N. Ann. Chim. Phys.* 27, 452; *Ann. Pharm.* 74, 306.

***Anisidine binitrique.***

*Formation* (p. 265).

*Preparation.* When ternitranisol is digested at a gentle heat with alcoholic hydrosulphate of ammonia, the liquid assumes a blood-red and afterwards a dark-brown colour, and finally solidifies. As soon as the action ceases, the liquid is heated to the boiling point, and evaporated to one-third, then supersaturated with dilute hydrochloric acid and filtered boiling hot. The clear brownish filtrate neutralised with ammonia becomes turbid and deposits dark red flakes, which are washed with water and dried in vacuo or over the water-bath.

*Properties.* Crystallises from solution in hot alcohol or ether in dark violet needles. When precipitated by ammonia from the hydrochlorate, it forms a crystalline powder, sometimes red, sometimes violet, according to the concentration of the liquid. Melts at a gentle heat, and solidifies on cooling in a blackish violet radiated mass resembling cinnabar.

| | | | Cahours. |
|---|---|---|---|
| 14 C | 84 | 39·43 | 39·34 |
| 3 N | 42 | 19·71 | 19·43 |
| 7 H | 7 | 3·28 | 3·35 |
| 10 O | 80 | 37·58 | 37·88 |
| $C^{14}N^3H^7O^{10}$ | 213 | 100·00 | 100·00 |

Fuming nitric acid decomposes it rapidly, forming an orange-yellow resinous mass which dissolves with deep brown colour in potash.

It dissolves very sparingly in cold water, somewhat more readily in boiling water, forming an orange-yellow solution.

Treated with excess of sulphuric, hydrochloric or nitric acid, it forms crystallisable salts which are decomposed by water, with separation of the base.

It dissolves sparingly in cold, better in boiling alcohol; sparingly in boiling ether.

## Benzonitranisidide.

$$C^{28}N^2H^{12}O^8 = C^{14}(C^{14}N^2H^7O^6)H^5O^2.$$

CAHOURS. *N. Ann. Chim. Phys.* 27, 456; *Ann. Pharm.* 74, 305; *J. pr. Chem.* 49, 271.

*Benzanisidide binitrique, Nitrobenzanisidide.*

*Formation* (p. 267).

*Preparation.* Nitranisidine is gradually heated with chloride of benzoyl; and the mass which solidifies after the action ceases, is repeatedly treated with water, hydrochloric acid and alkaline water, to remove nitranisidine and benzoic acid, and dissolved to saturation in boiling alcohol. As the solution cools, the compound crystallises out almost completely.

Light brown needles, which melt at a gentle heat, and volatilise at a higher temperature.

| | | | | Cahours. |
|---|---|---|---|---|
| 28 C | 168 | 61·76 | | 61·54 |
| 2 N | 28 | 10·29 | | 10·09 |
| 12 H | 12 | 4·41 | | 4·57 |
| 8 O | 64 | 23·54 | | 23·80 |
| $C^{28}N^2H^{12}O^8$ | 272 | 100·00 | | 100·00 |

Insoluble in water.

Dissolves in gently heated oil of vitriol, forming a dark red-brown solution.

Nearly insoluble in cold alcohol, but dissolves abundantly in hot alcohol, crystallising in needles on cooling.

Dissolves but sparingly in boiling ether, and separates as a crystalline powder on cooling.

## Phenetol.

$$C^{16}H^{10}O^2 = C^4H^5O,C^{12}H^5O.$$

CAHOURS. *Compt. rend.* 28, 586; *J. pr. Chem.* 47, 417.—*N. Ann. Chim. Phys.* 27, 463; *Ann. Pharm.* 74, 314; *J. pr. Chem.* 49, 283.—*Compt. rend.* 32, 60; *Ann. Pharm.* 78, 225; *Pharm. Centr.* 1849, 442, 75.

BALY. *Chem. Soc. Qu. J.* 2, 28; *Ann. Pharm.* 70, 269; *J. pr. Chem.* 47, 419.

*Phänäthol, Salithol, Carbolate of Ethyl, Carbolvinester.*—Discovered simultaneously by Cahours and by Baly in 1849.

*Formation and Preparation.* 1. By heating carbolate of potash with iodide of ethyl in a sealed tube to between 100° and 120°, or by distilling carbolate of potash with sulphovinate of potash. (Cahours.)—2. By heating ethylsalicylate of baryta by itself or ethylsalicylic acid with baryta. Ethylsalicylic acid is added by drops to anhydrous baryta, as long as any action takes place; the product distilled; and the distillate washed with alkaline water to remove carbolic acid, then dried over chloride of calcium, and rectified.

*Properties.* Transparent, colourless, very thin oil, lighter than water. Boils at 172° (Cahours), at 175° (Baly.) Has an agreeable aromatic odour.

| | | | | Cahours. | Baly. |
|---|---|---|---|---|---|
| 16 C | 96 | 78·68 | | 78·60 | 78·50 |
| 10 H | 10 | 8·18 | | 8·25 | 8·47 |
| 2 O | 16 | 13·14 | | 13·15 | 13·03 |
| $C^{16}H^{10}O^2$ | 122 | 100·00 | | 100·00 | 100·00 |

*Decompositions.* 1. Phenetol is violently attacked by *bromine*, with evolution of hydrochloric acid and formation of an oil, which, after a few days, solidifies in a crystalline mass. This substance may be crystallised from the solution and is found to consist of a number of substitution-products.

(Cahours, Baly.) Similarly with *chlorine.* — 2. It dissolves in fuming *nitric acid,* forming a liquid of a beautiful violet colour, which is destroyed by heating, binitrophenetol being then produced. (Baly.) It is violently attacked by fuming nitric acid; with an equal volume of the cold fuming acid, it forms a reddish liquid from which water throws down an oil, probably consisting of nitrophenetol, but not exhibiting a constant boiling point; when the liquid is boiled with a larger quantity of acid, binitrophenetol is produced. (Cahours.) — 3. Phenetol is not decomposed by boiling with potash-ley.

Phenetol dissolves pretty readily in *water.*

It dissolves in *oil of vitriol,* forming a conjugated acid which forms a crystallisable salt with baryta.

Mixes readily with *alcohol* and *ether.*

## Binitrophenetol.

$C^{16}N^2H^8O^{10} = C^4H^5O,C^{12}X^2H^3O.$

CAHOURS. *N. Ann. Chim. Phys.* 27, 465; *Ann. Pharm.* 74, 315; *J. pr. Chem.* 49, 284.

BALY. *Chem. Soc. Qu. J.* 2, 28; *Ann. Pharm.* 70, 269; *J. pr. Chem.* 47, 419.

*Binitrophänäthol, Dinitrosalithol, Binitrocarbolvinester.*

Phenetol is gradually mixed with an equal volume of fuming nitric acid and heated for a while to the boiling point, whereupon the dark brown liquid gradually becomes lighter, and on addition of water yields a yellow oil which soon becomes buttery and at length solidifies completely. The solid mass is repeatedly washed with water, pressed between paper, dissolved in boiling alcohol, and the solution left to cool. (Cahours, Baly.)

Yellow needles very much like binitranisol. When cautiously heated in small quantities, it sublimes without decomposition. (Cahours, Baly.)

| | | | Cahours. | Baly. |
|---|---|---|---|---|
| 16 C | 96 | 45·28 | 44·71 | 43·40 |
| 2 N | 28 | 13·21 | 13·03 | |
| 8 H | 8 | 3·77 | 4·03 | 3·77 |
| 10 O | 80 | 37·74 | 38·23 | |
| $C^{16}NH^8O^{10}$ | 212 | 100·00 | 100·00 | |

The compound appears to contain an admixture of ternitrophenetol. (Baly.) It appears to be converted into ternitrophenetol by boiling with excess of fuming nitric acid.

With hydrosulphate of ammonia, it yields nitrophenetidine.

## Nitrophenetidine.

$C^{16}N^{2}H^{10}O^{6} = C^{16}NXH^{18}O^{2}$.

CAHOURS. *Loc. cit.*

When sulphuretted hydrogen and ammonia are passed simultaneously through an alcoholic solution of binitrophenetol, sulphur is separated and nitrophenitidine remains dissolved in the alcohol.

Crystallises in brown needles resembling nitranisidine.

| | | | | Cahours. |
|---|---|---|---|---|
| 16 C | 96 | 52·74 | | 52·60 |
| 2 N | 28 | 15·39 | | |
| 10 H | 10 | 5·49 | | 5·41 |
| 6 O | 48 | 26·38 | | |
| $C^{16}N^{2}H^{10}O^{6}$ | 182 | 100·00 | | |

Forms crystallisable salts with sulphuric, hydrochloric and nitric acid.

Acts violently on chloride of benzoyl when heated with it, and forms a body which is very sparingly soluble in alcohol, and crystallises therefrom in small needles on cooling.

## Phenamylol.

$C^{22}H^{6}O^{2} = C^{10}H^{11}O,C^{12}H^{5}O$.

CAHOURS. *Compt. rend.* 32, 61; *Ann. Pharm.* 78, 227; *Pharm. Centr.* 1851, 166.

*Carbolate of Amyl, Carbolmylester.*

Obtained by heating carbolate of potash with iodide of amyl to between 100° and 120° in a sealed tube.

Transparent, colourless oil, boiling between 224° and 225°, and having an agreeable aromatic odour.

It is violently attacked by nitric acid and converted into a heavy oil which forms a crystallisable base with hydrosulphate of ammonia.

It dissolves in oil of vitriol, forming a red solution which is not precipitated by water, and forms a crystallisable salt with carbonate of baryta.

*Appendix to Salicylic Acid.*

## Ampelic Acid.

LAURENT. (1837.) *Compt. rend.* 4, 911.—*Ann. Chim. Phys.* 64, 325; *Rev. scient.* 6, 70; *J. pr. Chem.* 11, 418; *Pharm. Centr.* 1837, 522.

*Formation.* By the action of nitric acid on the portion of shale-oil which boils between 80 and 100°, or on the portion of coal-oil which boils between 130 and 160°.

*Preparation.* When that portion of coal-oil which boils between 130° and 160° is heated with commercial nitric acid, strong effervescence takes place; and if the addition of nitric acid be continued as long as red vapours escape, a slightly coloured solution is obtained together with a yellowish oil (the greater part of this oil is however carried forward with the vapours). The solution when evaporated, deposits crystals of picric acid, and yellow flakes which are partially separated by one or two crystallisations. The mother-liquor is neutralised with ammonia (potash would perhaps be preferable); the solution evaporated nearly to dryness; and the residue treated with alcohol, which dissolves the ampelate, leaving the greater part of the picrate undissolved. On evaporating the solution, digesting the residue in cold alcohol, again evaporating, dissolving the residue in water, and adding hydrochloric acid, a white flocculent precipitate of ampelic acid is produced, while traces of picric acid remain dissolved. The precipitate is washed and dried.

*Properties.* White. Separates from solution in hot alcohol or ether, in the form of a powder which has scarcely any crystalline character; inodorous. Melts below 200°, and distils undecomposed. — Reddens litmus.

| | | | |
|---|---|---|---|
| 14 C | 84 | 60·87 | 60·0 |
| 6 H | 6 | 4·35 | 4·4 |
| 6 O | 48 | 34·78 | 35·6 |
| $C^{14}H^{6}O^{6}$ | 138 | 100·00 | 100·0 |

Insoluble in cold, sparingly soluble in boiling *water*.

Dissolves in warm *oil of vitriol*, and is precipitated therefrom without alteration by water.

The ammonia-salt precipitates the salts of baryta, strontia and magnesia; with chloride of calcium, it forms at ordinary temperatures a white precipitate, which is not produced at higher temperatures; on cooling however the mixture deposits crystals. With acetate of nickel a greenish precipitate is formed; with acetate of lead, a white; with cupric acetate, a greenish blue, and with nitrate of silver a white precipitate. 100 pts. of the silver salt contain 4·46 pts. of silver.

The acid dissolves pretty readily in *alcohol* and *ether*.

## Oxybenzoic Acid.

GERLAND. (1853.) *Ann. Pharm.* 86, 143; 91, 189; *Pharm. Centr.* 1854, 829.

*Formation.* (p. 144).

*Preparation.* Nitrous acid is passed into a hot aqueous solution of amidobenzoic acid (p. 143) as long as bubbles of nitrogen continue to escape; on cooling, oxybenzoic acid crystallises out, and may be purified by boiling with water and animal charcoal.

*Properties.* Separates from the hot aqueous or alcoholic solution in the form of a colourless or yellowish crystalline powder. Melts at a

higher temperature and distils without alteration; volatilises even when the aqueous solution is boiled, passing over with the watery vapours, which deposit it on colder objects in needles having a strong lustre. — Reddens litmus strongly. Does not colour ferric salts.

| | | | Gerland. |
|---|---|---|---|
| 14 C | 84 | 60·87 | 60·99 |
| 6 H | 6 | 4·35 | 4·56 |
| 6 O | 48 | 34·78 | 34·45 |
| $C^{14}H^6O^6$ | 138 | 100·00 | 100·00 |

*Decompositions.* 1. When suddenly heated, it yields hydrate of phenyl and carbonic acid; and this decomposition takes place completely on heating the compound with excess of hydrate of lime. — 2. With nitric acid of sp. gr. 1·36, it gives off nitrous acid even at ordinary temperatures, and forms nitroxybenzoic acid.

*Combinations.* The acid dissolves sparingly in cold, abundantly in boiling *water*.

It expels carbonic acid from its compounds, and neutralises the alkalies. The alkaline oxybenzoates are easily soluble and difficult to crystallise; the oxybenzoates of the alkaline earths are less soluble and crystallise in needles. Those of the heavy metallic oxides are insoluble in water.

*Oxybenzoate of lead* is colourless.

| | | | Gerland. |
|---|---|---|---|
| PbO | 111·8 | 46·38 | 46·99 |
| $C^{14}H^5O^5$ | 129·0 | 53·62 | |
| $C^{14}H^5PbO^6$ | 240·8 | 100·00 | |

The acid dissolves sparingly in cold, readily in hot *alcohol*.

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## Sulphosalicol. $C^{14}H^6O^2,S^2$.

CAHOURS. *Compt. rend.* 25, 458.

*Thiosalicol.*

When an alcoholic solution of salicylimide is saturated with sulphuretted hydrogen, a white powder separates which may be washed with alcohol. — Colours ferric salts violet. Dissolves in alkalis.

## ¶. Sulphosalicylic Acid.

$C^{14}H^6S^2O^{12} = C^{14}H^6O^6,2SO^3$.

CAHOURS. *N. Ann. Chim. Phys.* 13, 93.
O. MENDIUS. *Ann. Pharm.* 103, 39.

**Discovered by Cahours; more particularly examined by Mendius.**

*Formation.* By the action of anhydrous sulphuric acid on salicylic acid.

*Preparation.* Perfectly dry salicylic acid is exposed to the vapour of anhydrous sulphuric acid in a capacious flask, cooled externally by water to prevent excessive rise of temperature. The crystals then become covered with a yellowish, transparent, viscid film, and by degrees the greater part of the acid is converted into a brownish gummy mass which envelopes the still unaltered crystals and protects them, to a great extent, from further action, so that, to render the transformation complete, a very large excess of anhydrous sulphuric acid is required. It is best therefore to stop the process when the action becomes very slow, dissolve out the sulphosalicylic acid by a small quantity of water, leave the liquid to cool, so that the remaining salicylic acid may be rendered nearly insoluble, saturate the filtrate with carbonate of baryta, with the aid of heat, and filter while still hot to separate sulphate of baryta. The solution on cooling deposits the greater part of the sulphosalicylate of baryta in crystals, the remainder of which may be obtained from the mother-liquor by repeated evaporation and crystallisation, and the crystals may be further purified by recrystallisation from hot water. — From the baryta-salt the free acid may be obtained by treating the solution, either with the exact quantity of sulphuric acid required to precipitate the baryta, — or by adding a slight excess of sulphuric acid, afterwards removing it by digestion with carbonate of lead, and precipitating the dissolved lead with sulphuretted hydrogen. — Or, again, the crude solution of sulphosalicylic acid and sulphuric acid may be treated at once with carbonate of lead, and the lead precipitated by sulphuretted hydrogen. — The solution of sulphosalicylic acid obtained by either of these methods may be evaporated without decomposition, even over the open fire; but to obtain distinct crystals, the concentrated solution must be left to evaporate over oil of vitriol; and to free the crystals from the red mother-liquor which adheres to them, they must be placed on a filter and left to stand over absolute alcohol, the vapour of which condenses on the crystals and carries the mother-liquor through the filter. (Mendius.)

*Properties.* Long, thin, silky needles radiating with great regularity from a centre; under the microscope, they present the appearance of irregular six-sided prisms, but without well-defined terminal faces. Melts at 120°, without decomposition and forms a radiated mass on cooling. Mendius.)

*Decompositions.* 1. The acid heated above 120° turns brown and decomposes, yielding hydrate of phenyl and a crystalline sublimate of salicylic acid [and giving off carbonic acid. ?]. — 2. It is not decomposed by heating with nitric or hydrochloric acid; but when it is boiled with a mixture of the two, the liquid becomes red and turbid and deposits on

cooling yellow crystalline flakes of chloranil (xi, 196). — 3. Sulphosalicylic acid heated with excess of sulphuric acid appears to yield bisulphocarbolic acid (xi, 168):

$$C^{14}H^6O^1,2SO^3 + 2SO^3 = C^{12}H^6O^2,4SO^3 + 2CO^2.$$

The gummy mass obtained by the action of anhydrous sulphuric on salicylic acid, was heated till it blackened and began to decompose, then treated with water, and the solution partially decolorised by digestion with carbonate of lead and subsequent precipitation of the lead by sulphuretted hydrogen. The filtrate neutralised with carbonate of baryta yielded when concentrated, a brown insoluble baryta-salt; and after the whole of this had been removed by repeated evaporation, the solution yielded with alcohol, a bulky, nearly white precipitate, which however turned brown in drying with the exception of a small portion. This latter was found to contain 37·05 p. c. barium, the formula of bisulphocarbolate of baryta requiring 35·2 p. c. and that of the sulphosalicylate, 38·8 p. c., whence it appears probable that the salt analysed was a mixture of sulphosalicylate and bisulphocarbolate of baryta. (Mendius.) [Was any evolution of carbonic acid observed in the reaction?] ¶.

*Combinations.* The acid dissolves in *water* in all proportions, and absorbs moisture from the air.

It is a bibasic acid, forming neutral salts, $C^{14}H^4M^2S^2O^{12}$, and acid salts, $C^{14}H^5MS^2O^{12}$. The neutral salts are obtained, either by decomposing the solution of the baryta-salt with the corresponding carbonates or sulphates, or by saturating the free acid with the oxides or carbonates.

The sulphosalicylates give off their water of crystallisation between 180° and 200°, but most of them bear a much higher temperature without decomposition. The neutral salts when subjected to dry distillation, give off phenylic alcohol; the acid salts yield in addition a sublimate of salicylic acid. They are all more or less soluble in water, but insoluble in alcohol and ether. The solutions impart to ferric salts a deep violet colour, but more inclining to red than that produced by salicylic acid. (Mendius.)

*Sulphosalicylate of Ammonia.*—Very unstable. Its solution when heated or left to evaporate spontaneously, quickly turns brown and gives off ammonia, and cannot be made to crystallise. By evaporation to dryness over the water-bath, a brown laminated mass is obtained, from which alcohol extracts a brown substance, but does not deposit it again on cooling (Mendius).

*Sulphosalicylate of Potash.* — *a. Neutral* or *Bibasic.* — Prepared by decomposing the baryta-salt with carbonate of potash, evaporating the filtrate to dryness, and crystallising from hot alcohol. — Small crystals generally without lustre, and arranged in branched groups, among which a few oblique prisms with dihedral summits may be distinguished. The salt is very soluble in water, forming a neutral solution, permanent in the air. Dissolves very sparingly in alcohol and ether. The crystals give off 10·45 p. c. (4 At.) water at 180°.

| *Crystallised.* | | | Mendius. |
|---|---|---|---|
| $C^{14}H^4S^2O^{12}$ | 216·0 | 65·37 | |
| 2 K | 78·4 | 23·73 | 23·34 |
| 4 HO | 36·0 | 10·90 | 10·58 |
| $C^{14}H^4K^2S^2O^{12} + 4Aq$ | 330·4 | 100·00 | |

*Acid* or *Monobasic.* — Obtained by neutralising the free acid with carbonate of potash, and mixing the solution with another equal quantity of the acid. Crystallises from the hot concentrated solution in rather

large spherical groups, consisting for the most part of very slender needles. The crystals when collected form a very light mass having a strong silky lustre. The crystals give off 12·14 p. c. In the moist state they easily turn red in contact with the air. They dissolve very readily in water but are insoluble in alcohol.

| | *Crystallised.* | | | Mendius. |
|---|---|---|---|---|
| $C^{14}H^5S^2O^{12}$ | 217·0 | .... | 74·27 | |
| K | 39·2 | .... | 13·41 | ..... 13·43 |
| 4 HO | 36·0 | .... | 12·32 | ..... 12·14 |
| $C^{14}H^5KS^2O^{12}$ + 4Aq | 292·2 | .... | 100·00 | |

*Sesquibasic.* — Crystallises from a mixture of the neutral salt with a quantity of the free acid smaller than that already contained in it, in very thin, light, radiating crystals having a strong silky lustre. They give off from 3·3 to 3·4 p. c. (2 At. water) at 200°.

| | *Crystallised.* | | | Mendius. | | |
|---|---|---|---|---|---|---|
| 28 C | 168·0 | .... | 29·52 | | | |
| 9 H | 9·0 | .... | 1·58 | | | |
| 3 K | 117·6 | .... | 20·63 | ..... 20·55 | .... | 20·64 |
| 4 S | 64·0 | .... | 11·24 | ..... 11· 6 | | |
| 24 O | 192·0 | .... | 33·69 | | | |
| 2 HO | 19·0 | .... | 3·34 | ..... 3· 3 | .... | 3· 4 |
| $C^{14}H^4K^2S^2O^{12}, C^{14}H^5KS^2O^{12}$ + 2Aq | 569·6 | .... | 100·00 | | | |

*Sulphosalicylate of Soda.* — *a. Neutral.* — Prepared like the potash-salt. Small, well defined, transparent and colourless crystals, having a strong glassy lustre, and the form of irregular six-sided prisms, sometimes with one oblique terminal face, sometimes with two, set at different angles. They are permanent in the air at ordinary temperatures; give off from 16 to 17 p. c. water (6 At.) at 200°; and when heated on platinum-foil, take fire and leave a carbonaceous residue. The salt is very soluble in water and forms a neutral solution; it is insoluble in alcohol and in ether, both of which liquids precipitate it after a while from the aqueous solution in crystalline flakes.

| | *At* 200°. | | | Mendius. |
|---|---|---|---|---|
| 14 C | 84·0 | .... | 32·06 | ..... 32·13 |
| 4 H | 4·0 | .... | 1·53 | ..... 1·93 |
| 2 Na | 46·4 | .... | 17·56 | ..... 17·59 |
| 2 S | 32·0 | .... | 12·21 | ..... 12·60 |
| 12 O | 96·0 | .... | 36·64 | ..... 35·75 |
| $C^{14}H^4Na^2S^2O^{12}$ | 262·4 | .... | 100·00 | ..... 100·00 |

| | *Crystallised.* | | | | | Mendius. | | |
|---|---|---|---|---|---|---|---|---|
| $C^{14}H^4S^2O^{12}$ | 216·0 | .... | 68·35 | | | | | |
| 2 Na | 46·4 | .... | 14·56 | ..... | 14·59 | | | |
| 6 HO | 54·0 | .... | 17·09 | ..... | 15·99 | .... 17·05 | .... | 16·9 |
| $C^{14}H^4Na^2S^2O^{12}$ + 6Aq | 316·4 | .... | 100·00 | | | | | |

*b. Acid.* — Prepared like the acid potash-salt. Very light, thin rhombic laminæ, having a silky lustre and permanent in the air. Give off 12·8 p. c. (4 At.) water at 180°. Easily soluble in water, sparingly in alcohol.

| | *Crystallised.* | | | Mendius. |
|---|---|---|---|---|
| $C^{14}H^5S^2O^{12}$ | 217·0 | | | |
| Na | 23·2 | 9·30 | | 8·2 |
| 4 O | 36·0 | 13·05 | | 12·8 |
| $C^{14}H^5NaS^2O^{12}$ + 4Aq | 276·2 | | | |

*Sulphosalicylate of Potash and Soda.* — Obtained by neutralising the acid potash-salt with carbonate of soda. From a very concentrated hot solution, it crystallises on cooling in small rectangular prisms bevelled with two equally inclined faces, and having a strong silky lustre. Soluble in water, but insoluble in alcohol and ether. They give off 20·48 p. c. (8 At.) water at 200°.

| | *Crystallised.* | | | Mendius. |
|---|---|---|---|---|
| $C^{14}H^4S^2O^{12}$ | 216·0 | | | |
| K | 39·2 | 11·19 | | 11·16 |
| Na | 23·2 | 6·57 | | 6·68 |
| 8 HO | 72·0 | 20·56 | | 20·48 |
| $C^{14}H^4KNaS^2O^{12}$ + 8Aq | 350·4 | | | |

*Sulphosalicylate of Baryta.* — *a.* — *Neutral.* — *Preparation,* (p. 275.) — Forms three different kinds of crystals, all of which have however the same composition: *a.* Soft light silky needles, either united in concentric groups; or if very gradually formed, in larger tuft-like or sheave-like groups. This was the usual form of the first crop of crystals from the hot aqueous solution. — (*β.*) Small hard crystals mostly in concentric groups, and having their free extremities acuminated with four faces, set at unequal angles on the four lateral faces of an oblique prism. These were obtained only in one preparation. The hot filtrate of the baryta-salt solidified on that occasion into a compact jelly which yielded, by recrystallisation, very soft light needles; and when these were dissolved in the smallest possible quantity of water, for the purpose of decolorising them, a considerable quantity of the salt separated out as soon as the liquid boiled, and to redissolve it, a larger quantity of water was required. This solution on cooling yielded the hard crystals just mentioned. — *γ.* Small soft roundish nodules, which under the microscope appeared to be composed of small concentrically grouped needles. These were obtained from the mother-liquors after repeated evaporation. All these crystals contained about 13 per cent. (6 At.) water, of which 5 At. were given off at 150° and the remainder between 180° and 200°. The salt sustains a tolerably high temperature without decomposition, but when more strongly heated, it chars and gives off hydrate of phenyl. It dissolves sparingly in cold, readily in hot water, but is perfectly insoluble in alcohol and ether.

| | *At* 200°. | | | Mendius. |
|---|---|---|---|---|
| 14 C | 84·0 | 23·80 | | 23·85 |
| 4 H | 4·0 | 1·13 | | 1·55 |
| 2 Ba | 137·2 | 38·80 | | 38·82 |
| 2 S | 32·0 | 9·10 | | 9·40 |
| 12 O | 96·0 | 27·17 | | 26·38 |
| $C^{14}H^4Ba^2S^2O^{12}$ | 353·2 | 100·00 | | 100·00 |

| | Crystallised. | | | Mendius. α. | | β. | | γ. |
|---|---|---|---|---|---|---|---|---|
| $C^{14}H^4S^2O^{12}$ | 216·0 | .... | 53·08 | | | | | |
| 2 Ba | 137·2 | .... | 33·66 | ..... | 33·6 | .... | 33·8 | .... | 33·6 |
| 6 HO | 54·0 | .... | 13·26 | ..... | 13·1 | .... | 12·9 | .... | 13·1 |
| $C^{14}H^4Ba^2S^2O^{12}$ + 6Aq | 407·2 | .... | 100·00 | | | | | |

Sulphosalicylic acid does not appear to be capable of taking up more than 2 atoms of a base. Hot concentrated solutions of the preceding salt and caustic baryta mixed together, did not yield any crystals on cooling; and on adding alcohol to the clear solution left after all the excess of baryta had been removed as carbonate by exposure to the air, a fine light powder was thrown down, still exhibiting the composition of the bibasic salt (Mendius).

*b. Acid.* — Obtained by precipitating the baryta from a portion of the salt *a* with sulphuric acid, and mixing the filtrate with an equal portion of the same salt. Crystallises in well defined, oblique, irregular six-sided prisms, perfectly transparent, having a strong glassy lustre, and permanent in the air. At 200°, they give off 11·17 p. c. (4 At.) water. They dissolve readily in water, but are insoluble in alcohol or ether.

| | Crystallised. | | | Mendius. | |
|---|---|---|---|---|---|
| $C^{14}H^5S^2O^{12}$ | 217·0 | .... | 67·50 | | |
| Ba | 68·6 | .... | 21·31 | ..... | 21·32 |
| 4 HO | 32·0 | .... | 11·19 | ..... | 11·17 |
| $C^{14}H^5BaS^2O^{12}$ + 4Aq | 317·6 | .... | 100·00 | | |

*Sulphosalicylate of Lime.* — The hot aqueous solution of the acid, saturated with carbonate of lime, yields very small, light, silky needles united in hemispherical groups. They give off 6·43 p. c. (2 At.) water at 200°. They are soluble in water, but insoluble in alcohol and ether, which indeed precipitate the salt from its aqueous solution.

| | Crystallised. | | | Mendius. | |
|---|---|---|---|---|---|
| $C^{14}H^4S^2O^{12}$ | 216 | .... | 78·84 | | |
| 2 Ca | 40 | .... | 14·59 | ..... | 14·51 |
| 2 HO | 18 | .... | 6·57 | ..... | 6·43 |
| $C^{14}H^4Ca^2S^2O^{12}$ + 2Aq | 274 | .... | 100·00 | | |

*Sulphosalicylate of Magnesia.* — Prepared like the lime-salt. Crystallises in rather long rectangular prisms irregularly crossing each other; they have but little lustre, which they lose when exposed to the air. At 200°, they give off 18·24 p. c. (6 At.) water. The salt is so very soluble in water that it can be crystallised only by evaporation of a concentrated solution over oil of vitriol; it is insoluble in alcohol. The solution forms with phosphate of soda an immediate precipitate, but if ammonia and sal-ammoniac be previously added, the precipitate forms only on boiling, and partially redissolves on cooling.

| | Crystallised. | | | Mendius. | |
|---|---|---|---|---|---|
| $C^{14}H^4S^2O^{12}$ | 216 | .... | 73·44 | | |
| 2 Mg | 24 | .... | 8·16 | ..... | 8·10 |
| 6 HO | 54 | .... | 18·40 | ..... | 18·24 |
| $C^{14}H^4Mg^2S^2O^{12}$ + 6Aq | 294 | .... | 100·00 | | |

*Sulphosalicylate of Zinc.* — Obtained by decomposing the baryta-salt with sulphate of zinc. Resembles the magnesia-salt in crystalline form, solubility, and the change which it undergoes on exposure to the air. May be set on fire and burns with a bright light. Gives off 16·03 p. c. (6 At.) water at 200°.

| | *Crystallised.* | | | Mendius. |
|---|---|---|---|---|
| $C^{14}H^4S^2O^{12}$ | 216·0 | .... | 74·27 | |
| 2 Zn | 64·4 | .... | 13·41 | ..... 13·43 |
| 6 HO | 54·0 | .... | 12·32 | ..... 12·14 |
| $C^{14}H^4Zn^2S^2O^{12}$ + 6Aq | 334·4 | .... | 100·00 | |

*Sulphosalicylate of Lead.* — The hot aqueous acid saturated with carbonate of lead, yields small, indistinct, round nodules. The salt melts when heated and swells up; may be set on fire and continues to glow. Sparingly soluble in water, insoluble in alcohol, which precipitates it in flakes even from a dilute aqueous solution.

| | | | | Mendius. | |
|---|---|---|---|---|---|
| $C^{14}H^4S^2O^{12}$ | 216 | .... | 51·04 | | |
| 2 Pb | 207·2 | .... | 48·96 | ..... 48·79 | .... 49·05 |
| $C^{14}H^4Pb^2S^2O^{12}$ | 423·2 | | 100·00 | | |

*Sulphosalicylate of Copper.* — *a. Basic.* — Recently precipitated cupric hydrate, digested in excess with the aqueous acid, forms a solution of an intense olive-green colour, which refuses to crystallise, but when evaporated over the water-bath, leaves a heavy bright green powder covered with a viscid varnish. This residue is completely insoluble in alcohol, but water dissolves the varnish, forming an uncrystallisable, strongly acid solution. — The green powder which, under the microscope, presents the appearance of small stellate needles, is a basic salt, which gives off 9·06 p. c. (4 At.) water at 180°.

| | *Green powder.* | | | Mendius. |
|---|---|---|---|---|
| $C^{14}H^4S^2O^{12}$ | 216·0 | .... | 57·09 | |
| 4 Cu | 126·4 | .... | 33·40 | ..... 31·6 |
| 4 HO | 36·0 | .... | 9·51 | ..... 9·1 |
| $2CuO,C^{14}H^4Cu^2S^2O^{12}$ + 4Aq | 378·4 | .... | 100·00 | |

*b. Neutral.* — Obtained by decomposing the baryta-salt with sulphate of copper. The filtrate highly concentrated and left to evaporate in vacuo, deposits green cauliflower-like masses which exhibit a crystalline structure under the microscope. Permanent in the air, very soluble in water, sparingly soluble in alcohol, the small quantity dissolved in the hot liquid separating again in the form of a jelly on cooling.

| | *At* 180°. | | | Mendius. |
|---|---|---|---|---|
| $C^{14}H^4S^2O^{12}$ | 216·0 | .... | 77·36 | |
| 2 Cu | 63·2 | .... | 22·64 | ..... 22·42 |
| $C^{14}H^4Cu^2S^2O^{12}$ | 279·2 | .... | 100·00 | |

*Sulphosalicylate of Silver.* — Obtained by adding recently precipitated oxide of silver in excess to a hot solution of sulphosalicylic acid, which quickly dissolves it. The hot concentrated solution solidifies on cooling, into a stiff jelly, which disappears after some time, the salt falling to the bottom in the form of a heavy powder, composed of perfectly rounded spherules, which when crushed, exhibit under the microscope an appearance of crystallisation. The salt gives off 3·9 p. c. (2 At.) water at 150°, melts at a higher temperature, and decomposes with strong intumescence. It dissolves sparingly in cold, readily in hot water, but is insoluble in alcohol. The solution boiled for some time deposits metallic silver.

| | *Crystallised.* | | | Mendius. | |
|---|---|---|---|---|---|
| $C^{14}H^4S^2O^{12}$ | 216 | 48 | | | |
| 2 Ag | 216 | 48 | | 47·7 | 48·1 |
| 2 HO | 18 | 4 | | 3·9 | |
| $C^{14}H^4Ag^2S^2O^{12}$ | 450 | 100 | | | |

Sulphosalicylic acid dissolves in all proportions in *alcohol* and in *ether*. (Mendius.)

## ¶. Sulphosalicylate of Ethyl.

$$C^{22}H^{14}S^2O^{12} = 2C^4H^5O,C^{14}H^4S^2O^{10}.$$

MENDIUS. *Ann. Pharm.* 103, 62.

*Preparation.* Perfectly dry sulphosalicylate of silver is agitated with an equivalent quantity of iodide of ethyl, either in a sealed tube or in an open flask; and after the action, which is attended with moderate evolution of heat, has extended throughout the entire mass, the product is exhausted with ether and the ethereal solution left to evaporate at a gentle heat; any excess of iodide of ethyl then escapes together with the ether, and sulphosalicylate of ethyl remains in the form of crystalline crusts, which remain moist and gummy even after standing for some time; it may be purified by recrystallisation from a small quantity of warm alcohol. The formation of this compound is represented by the equation:

$$C^{14}H^4Ag^2S^2O^{12} + 2C^4H^5I = 2AgI + C^{14}H^4(C^4H^5)^2S^2O^{12}.$$

It is not produced by passing hydrochloric acid gas into an alcoholic solution of the acid.

*Properties.* Small, dazzling white, silky crystals, which under the microscope, look very much like the ordinary crystals of sulphate of lime. They are soft to the touch and become soft and kneadable like wax, even by pressure between the fingers. The compound melts without decomposition at 56°, and remains soft and pasty even after cooling considerably below that temperature. It melts under water at the same temperature, and may be distilled over unaltered with the water. It is perfectly neutral, both to litmus and to carbonate of soda.

| | | | Mendius. |
|---|---|---|---|
| 22 C | 132 | 48·1 | 47·7 |
| 14 H | 14 | 5·1 | 5·2 |
| 2 S | 32 | 11·7 | 11·8 |
| 12 O | 96 | 35·1 | 35·3 |
| $C^{22}H^{14}S^2O^{12}$ | 274 | 100·0 | 100·0 |

When an alcoholic solution of the compound was heated for two or three hours in a sealed tube with alcoholic ammonia, and the alcohol afterwards distilled off, a brown syrup remained, which was soluble in water, insoluble in ether, had an ammoniacal odour and neutral reaction.

Sulphosalicylate of ethyl is insoluble in water, but dissolves readily in *alcohol* and in *ether;* from the alcoholic solution it is precipitated by water: (Mendius.) ¶.

*Oxygen-nucleus* $C^{14}H^5O^2$.

## Anhydrous Salicylic Acid.

$C^{14}H^5O^5 = C^{14}H^5O^3,O^2$.

GERHARDT. *N. Ann. Chim. Phys.* 37, 322; *Ann. Pharm.* 87, 158; *J. pr. Chem.* 61, 300.

*Salicylic Anhydride, Salicylic Salicylate, Salicylate of Salicyl.*

Produced by the action of chlorophosphoric acid on dry salicylate of soda. The action is always attended with evolution of hydrochloric acid, even when the two bodies are mixed in equivalent proportions (1 At. chlorophosphoric acid to 6 At. salicylate of soda), salicylide being formed at the same time. The product is very hard and adheres closely to the vessel, but when heated with water, it becomes soft and tenacious and solidifies after some time only. Boiling alcohol extracts anhydrous salicylic acid from it, and the solution on cooling yields a thick oil which solidifies after some time. The solution in boiling ether yields the acid on cooling, in the form of a flexible mass. With boiling water it yields salicylic acid; with alkalis, a salicylate.

## Acetic Salicylate.

$C^{18}H^8O^6 = C^{14}H^5O^5,C^4H^3O^3$.

Chloride of acetyl ($C^4H^3O^2Cl$), acts violently at ordinary temperatures on salicylate of soda, the mixture first becoming liquid but solidifying after a short time. The product treated with a dilute solution of carbonate of soda, froths up and yields salicylate and acetate of soda. (Gerhardt.)

## Benzoic Salicylate.

$C^{28}H^{10}O^{6} = C^{14}H^{5}O^{5},C^{14}H^{5}O^{3}$.

*Benzosalicylic Anhydride, Anhydrous Benzo-salicylic acid.*

Produced by the action of chloride of benzoyl on salicylate of soda.

Flexible mass difficult to purify. Boiling water converts it into hydrated benzoic and salicylic acids. When heated, it yields benzoate of phenyl and bodies soluble in potash. (Gerhardt.)

*Appendix.*

## Salicylide. $C^{14}H^{4}O^{4}$.

GERHARDT & SOCOLOFF. (1852.) *N. Ann. Chim. Phys.* 37, 323; *Ann. Pharm.* 87, 159; *J. pr. Chem.* 61, 300.

Produced by the action of chlorophosphoric acid on salicylate of soda, and contained in the residue which is insoluble in boiling alcohol.

$$4C^{14}H^{5}NaO^{6} + PO^{2}Cl^{3} = 2C^{14}H^{5}O^{6} + C^{14}H^{4}O^{4} + NaCl + 3NaO,PO^{5} + 2HCl.$$

White amorphous powder, not attacked by boiling water, sparingly soluble in boiling alcohol, insoluble in ether. Melts to a transparent liquid when heated, and remains transparent after solidification. — With potash-ley, it rather quickly forms salicylate of potash. It is slowly altered by boiling with caustic ammonia, but remains unaltered when boiled with carbonate of soda.

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*Thio-nucleus* $C^{14}H^{7}(SO^{2})$.

## Thiotoluol or Sulphotoluol.

$C^{14}H^{7}SO^{2} = C^{14}H^{7}(SO^{2})$.

DEVILLE. *N. Ann. Chim. Phys.* 3, 172.

Produced in very small quantity by the action of fuming sulphuric acid on toluol, and remains in shining crystals when the sulphotoluic acid is dissolved out of the resulting crystalline mass (p. 230).

*Oxyiodine-nucleus* $C^{14}IH^{5}O^{2}$.

## Iodosalicylous Acid.

$C^{14}IH^{5}O^{4} = C^{14}IH^{5}O^{2},O^{2}$.

LÖWIG. (1835.) *Pogg.* 36, 403; *Pharm. Centr.* 1836, 62.

*Iodide of Spiroyl, Iodide of Salicyl.*

When bromospiroylous or chlorospiroylous acid is heated with iodide of potassium, iodosalicylous acid sublimes.

Solid, dark brown, easily fusible mass, which with water, alcohol, ether, and salifiable bases, exhibits reactions similar to those of bromosalicylous or chlorosalicylous acid.

*Oxybromine-nucleus* $C^{14}BrH^5O^2$.

## Bromosalicylous Acid.

$C^{14}BrH^5O^4 = C^{14}BrH^5O^2,O^2$.

PAGENSTECHER. (1834.) *Repert.* 49, 345.
LÖWIG. *Pogg.* 36, 401; *Pharm. Centr.* 1836, 63.
PIRIA. *Ann. Pharm.* 30, 171; *Ann. Chim. Phys.* 69, 281; *Pharm. Centr.* 1839, 375.
LÖWIG & WEIDMANN. *Pogg.* 46, 57; *Pharm. Centr.* 1839, 131.
HEERLEIN. *J. pr. Chem.* 32, 65; *Pharm. Centr.* 1844, 598.
BERTAGNINI. *Ann. Pharm.* 85, 196.

***Bromide of Salicyl, Bromide of Spiroyl, Bromospiroylous acid.***

*Formation.* By the action of bromine on salicylous acid at ordinary temperatures (p. 338).

*Preparation.* 1. When bromine is brought in contact with salicylous acid, the mixture becomes very hot, hydrobromic acid is evolved, and on cooling, the whole solidifies in a crystalline mass, which may be purified by crystallisation from alcohol. (Löwig, Piria.) Löwig & Weidmann allow the vapour of bromine to act upon the acid at ordinary temperatures, in a bottle filled with bromine-vapour, for example. — 2. Aqueous salicylous acid is shaken with bromine-water, and the flakes which separate are purified by keeping them in the melted state over the water-bath as long as hydrobromic acid continues to escape. (Löwig.) — 3. Bromine is added, not in excess, to the alcoholic solution of salicylous acid; and the mixture immediately diluted with a large quantity of cold water; a resinous body is then precipitated which instantly solidifies, while flakes continue to float in the liquid. The resinous body is dissolved in alcohol, and on leaving the solution to evaporate spontaneously, bromosalicylous acid crystallises out first. (Heerlein.)

*Properties.* Small colourless needles. (Piria, Löwig & Weidmann.) Yellowish crystals which look like square prisms when examined by the microscope, but have a woolly aspect when seen in mass. (Heerlein.) Melts at the heat of the water-bath, forming a colourless liquid which solidifies in the crystalline form. May be sublimed without decomposition. Volatilises undecomposed when boiled with water. (Löwig.) Smells like benzoïn. The alcoholic solution decolorises litmus and indigo. (Heerlein.)

| | | | Löwig. | Piria. | Löwig & Weidmann. | Heerlein. |
|---|---|---|---|---|---|---|
| 14 C | 84 | 41·79 | 37·86 | 42·19 | 40·49 | |
| 5 H | 5 | 2·48 | 2·67 | 2·53 | 2·89 | |
| Br | 80 | 39·80 | 40·50 | 39·18 | 40·92 | 39·45 |
| 4 O | 32 | 15·93 | 18·97 | 16·10 | 15·79 | |
| $C^{14}BrH^5O^4$ | 201 | 100·00 | 100·00 | 100·00 | 100·00 | |

The alcoholic solution saturated at the boiling heat with sulphuretted hydrogen, assumes a reddish colour and precipitates sulphur. The absorption is accelerated by addition of ammonia. Water then precipitates sulphide of bromosalicene. (Heerlein.)

With ammonia and salifiable bases, the acid behaves likes chlorosalicylous acid.

The alkaline bromosalicylites are less soluble in water [than the chlorosalicylites?]. The baryta-salt contains 28·46 p. c. (1 At.) of baryta. (Löwig & Weidmann.)

With bisulphite of potash, the acid forms a compound which crystallises in needles, and with bisulphite of soda, small aggregated needles. Both compounds dis olve readily in water and are decomposed by heat or by the action of acids.

Insoluble in water. Dissolves readily in *alcohol* and *ether*.

## Bromosalicylic Acid.

$C^{14}BrH^5O^6 = C^{14}BrH^5O^2,O^4$.

GERHARDT. (1842.) *N. Ann. Chim. Phys.* 7, 217; *Rev. scient.* 10, 216; *Ann. Pharm.* 45, 21; *Pharm. Centr.* 1843, 169.

CAHOURS. *N. Ann. Chim. Phys.* 13, 99; *Ann. Pharm.* 52, 342; *J. pr. Chem.* 35, 90; *Pharm. Centr.* 1845, 884.

***Acide Monobromosalicylique, Bromsalicylsäure.***

*Formation.* By the action of bromine on excess of salicylic acid.

*Preparation.* Pulverised salicylic acid is gradually triturated with a quantity of bromine, such that part of the acid remains unaltered; the brown gummy mass is washed with small quantities of cold alcohol, which extracts the unaltered acid; the residue dissolved in boiling alcohol; and the solution left to evaporate.

Colourless prisms having a strong lustre, and somewhat like salicylic acid; they melt when slightly heated.

| | | | Gerhardt. | Cahours. |
|---|---|---|---|---|
| 14 C | 84 | 38·70 | 39·2 | 39·78 |
| 5 H | 5 | 2·30 | 2·3 | 2·62 |
| Br | 80 | 36·86 | | 36·02 |
| 6 O | 48 | 22·14 | | 21·58 |
| $C^{14}H^5BrO^6$ | 217 | 100·00 | | 100·00 |

Decomposed by dry distillation. When distilled with fine sand and a small quantity of baryta, it yields thick vapours, condensing into a reddish liquid, which, by repeated distillation with sand and baryta, yields bromocarbolic acid:

$$C^{14}BrH^5O^6 = C^{12}BrH^5O^2 + 2CO^2.$$

Bromosalicylic acid dissolves but very sparingly in water, even at the boiling heat. With ammonia, potash and soda, it forms crystallisable salts, which are less soluble in water than the salicylates. — It colours ferric salts red, like salicylic acid.

It dissolves pretty readily in *alcohol* and *ether*, especially when warm.

## Methylbromosalicylic Acid.

$C^{16}BrH^7O^6 = C^2H^3O,C^{14}BrH^4O^5$.

CAHOURS. (1844.) *N. Ann. Chim. Phys.* 10, 339; *Pharm. Centr.* 1844, 437.

*Salicylate de methyle monobromé, Methylbromsalicylsäure, Bromsalicylformester.*

When bromine is slowly dropped into methylsalicylic acid kept as cold as possible, and the mass which solidifies on cooling is freed from hydrobromic acid by washing with weak alcohol, and dissolved in boiling alcohol of 36°, the liquid as it cools deposits shining crystalline laminæ of methylbibromosalicylic acid, an additional quantity of which is obtained from the mother-liquor on cooling, after evaporation to one-half. The remaining mother-liquor however yields by further evaporation, crystals of methylbromosalicylic acid, which may be purified by three crystallisations from alcohol or by sublimation.

Silky needles having a peculiar odour and melting at 55°. Sublimes without decomposition.

| | | | Cahours. |
|---|---|---|---|
| 16 C | 96 | 41·56 | 41·69 |
| 7 H | 7 | 3·03 | 3·17 |
| Br | 80 | 34·63 | 34·30 |
| 6 O | 48 | 20·78 | 20·84 |
| $C^{16}H^7BrO^6$ | 231 | 100·00 | 100·00 |

The acid dissolves in hot potash-ley, forming bromosalicylate of potash. In contact with ammonia, it disappears after some time only. Mineral acids added to the solution throw down white flakes, which crystallise from hot alcohol. The ammoniacal solution, evaporated and subjected to dry distillation, yields, first ammonia and then salhydramide. Distilled with cyanide of mercury, it forms a compound in which the bromine is replaced by cyanogen.

With cold strong potash-ley, it forms a compound similar to that which is formed by methylsalicylic acid, and very soluble in acetic acid; the solution mixed with water, exhibits a milky turbidity, and after a while deposits the unaltered substance in needles having a silky lustre.

Dissolves in *alcohol* and readily in *ether*.

## Ethylbromosalicylic Acid.

$C^{18}BrH^9O^6 = C^4H^5O,C^{14}BrH^4O^5$.

CAHOURS. (1844.) *N. Ann. Chim. Phys.* 10, 341.

Produced by the action of bromine on ethylsalicylic acid, the latter being in excess. Dissolves very easily in alcohol, and crystallises therefrom in slender needles, very much like methylbromosalicylic acid.

## Sulphide of Bromosalicene.

$C^{14}BrH^5O^2S^2 = C^{14}BrH^5O^2,S^2$.

HEERLEIN. (1838.) *J. pr. Chem.* 32, 68; *Pharm. Centr.* 1844, 599.

Sulphuretted hydrogen is passed to saturation through a boiling solution of bromosalicylous acid, (the absorption is somewhat accelerated by addition of ammonia), the liquid mixed with water, and the resulting brown resinous precipitate purified by repeated solution in alcohol and precipitation by water; it is then dried over the water-bath, whereupon the mass which was tenacious at first, becomes perfectly brittle.

Amorphous. Melts somewhat below 100°. Not volatile.

| | | | Heerlein. |
|---|---|---|---|
| 14 C | 84 | 38·71 | 40·10 |
| Br | 80 | 36·87 | 34·94 |
| 5 H | 5 | 2·30 | 2·94 |
| 2 O | 16 | 7·37 | 6·74 |
| 2 S | 32 | 14·75 | 15·28 |
| $C^{14}BrH^5S^2O^2$ | 217 | 100·00 | 100·00 |

Resolved by dry distillation into empyreumatic substances containing sulphur.

Dissolves in potash and is precipitated therefrom by acids, with evolution of a small quantity of sulphuretted hydrogen.

*Oxybromine-nucleus* $C^{14}Br^2H^4O^2$.

## Bibromosalicylous Acid.

$C^{14}Br^2H^4O^4 = C^{14}Br^2H^4O^2,O^2$.

HEERLEIN. *J. pr. Chem.* 32, 65; *Pharm. Centr.* 1844, 598.

*Bibromide of Spiroyl, Zweifachbromspiroyl.*

*Preparation.* When bromine-water is added to an aqueous solution of salicylous acid till the colour becomes permanent, a white crystallo-flocculent precipitate is formed, while lighter flocks remain suspended in the liquid. The precipitate melts together when heated in the water-bath, and solidifies on cooling; the alcoholic solution left to evaporate spontaneously, first yields crystals of bibromosalicylous acid, but afterwards bromosalicylous acid likewise separates from it. — When bromine is added to an alcoholic solution of salicylous acid till the colour becomes permanent, or when the resinous mass obtained in the preparation of bromosalicylous acid (p. 284) is dissolved in alcohol, and bromine added in excess, the mixture becomes heated, and yields on cooling crystals of bibromosalicylous acid. Löwig & Weidmann obtained in the same manner, or by treating the oily acid with bromine at the heat of the water-bath, mixtures of bromosalicylous and bibromosalicylous acid. (*Pogg.* 46, 57.)

*Properties.* Yellowish, very long needles consisting of microscopic square prisms. Melts at the heat of the water-bath. Has a peculiar odour like that of gum benzoïn. The alcoholic solution decolorises litmus and indigo.

| | | | Heerlein. |
|---|---|---|---|
| 14 C | 84 | 30·00 | 29·52 |
| 4 H | 4 | 1·43 | 1·87 |
| 2 Br | 160 | 57·13 | 56·78 |
| 4 O | 32 | 11·44 | 11·83 |
| $C^{14}Br^2H^4O^4$ | 280 | 100·00 | 100·00 |

Treated with bromine for some time in sunshine and with the aid of heat, it yields a body containing 67·12 per cent. of bromine. (Löwig & Weidmann, compare p. 238). — When sulphuretted hydrogen is passed for some hours through a warm alcoholic solution of the acid mixed with a little ammonia, a brown resinous mass separates consisting of sulphide of bromosalicene. (Heerlein.)

Bibromosalicylous acid unites with salifiable bases. When its solution in potash-ley is evaporated and heated, the residue becomes red-hot sooner than the vessel. (Heerlein.)

Insoluble in water, but soluble in *alcohol* and *ether*.

## Bibromosalicylic Acid.

$C^{14}Br^2H^4O^6 = C^{14}Br^2H^4O^2,O^4$.

CAHOURS. (1845.) *N. Ann. Chim. Phys.* 13, 102; *Ann. Pharm.* 52, 333; *J. pr. Chem.* 35, 82; *Pharm. Centr.* 1845, 884.

*Formation.* By the action of bromine in excess on salicylic acid.

*Preparation.* 1. Pulverised salicylic acid is gradually triturated with excess of bromine as long as any action takes place, and the mixture is left to stand for some hours; the excess of bromine is then washed out with cold water, and the residue dissolved in boiling ammonia. As the solution cools, the ammonia-salt is deposited in slender shining needles. These crystals are dissolved in water; the acid precipitated by hydrochloric acid; the white precipitate washed and dissolved in boiling alcohol; and the solution left to evaporate. — 2. When bromine is dissolved in a concentrated solution of salicylate of potash, the liquid becomes heated and soon deposits crystals of bibromosalicylate of potash; this salt is decomposed by hydrochloric acid, and the separated acid washed and crystallised from alcohol.

Short colourless or slightly reddish needles which melt at about 150°.

| | | | Cahours. (1.) | (2). |
|---|---|---|---|---|
| 14 C | 84 | 28·38 | 28·66 | 28·19 |
| 4 H | 4 | 1·35 | 1·62 | 1·54 |
| 2 Br | 160 | 54·05 | 53·20 | 53 56 |
| 6 O | 48 | 16·22 | 16·52 | 16·71 |
| $C^{14}H^4Br^2O^6$ | 296 | 100·00 | 100·00 | 100·00 |

Distilled with sand and a small quantity of baryta, it yields bibromocarbolic acid. — It dissolves readily in boiling nitric acid of 36°, giving off nitrous vapours and bromine-vapours, and yielding crystals of picric acid as it cools.

Dissolves sparingly in water. Dissolves in gently heated oil of vitriol and is precipitated therefrom by water.

The bibromosalicylates of ammonia, potash and soda are even less soluble than the bromosalicylates. The potash-salt crystallises from alcohol in shining colourless prisms.

The acid dissolves pretty readily in *acetic acid*, still more readily in *ether*.

## Methylbibromosalicylic Acid.

$C^{16}Br^2H^6O^6 = C^2H^3O,C^{14}Br^2H^3O^5$.

CAHOURS. (1844.) *N. Ann. Chim. Phys.* 10, 341.

*Bibromsalicylformester.*

The first crystals which separate from the alcoholic solution of the mass obtained by treating methylsalicylic acid with bromine, are crystallised from hot alcohol. The compound is also formed when methylbromosalicylic acid is brought in contact with bromine, the mixture becoming hot and giving off hydrobromic acid.

Shining prisms, which melt at 145° and volatilise at a higher temperature.

| | | | Cahours. |
|---|---|---|---|
| 16 C | 96 | 30·97 | 31·29 |
| 6 H | 6 | 1·94 | 2·04 |
| 2 Br | 160 | 51·61 | 51·43 |
| 6 O | 48 | 15·48 | 15·24 |
| $C^{16}H^6Br^2O^6$ | 310 | 100·00 | 100·00 |

The solution of the acid in very strong potash-ley assumes a yellow colour when heated, and acids separate white flakes from it, which no longer exhibit the properties of methylbibromosalicylic acid. It dissolves sparingly in bromine, remaining unaltered and in large laminæ when the solvent evaporates. With cyanide of mercury it behaves in a similar manner to methylbromosalicylic acid (p. 286).

It dissolves in cold potash or soda-ley, forming crystallisable compounds, and is separated again by acids in its original state.

It is insoluble in water, but dissolves readily in *alcohol* and *ether* especially when heated.

## Ethylbibromosalicylic Acid.

$C^{18}Br^2H^8O^6 = C^4H^5O,C^{14}Br^2H^3O^5$.

CAHOURS. (1844.) *N. Ann. Chim. Phys.* 10, 364.

*Bibromsalicylvinester.*

Ethylbromosalicylic acid becomes heated by contact with bromine, giving off hydrobromic acid and forming ethylbibromosalicylic acid, which crystallises from solution in boiling alcohol in large scales having a pearly lustre. Melts when slightly heated, and on cooling solidifies in a crystalline mass, the form of which resembles that of bismuth. With 10 or 15 grms. of substance, very fine cubes are obtained. The acid when carefully heated, volatilises almost without residue and forms a crystalline sublimate.

| | | | Cahours. |
|---|---|---|---|
| 18 C | 108 | 33·33 | 33·34 |
| 8 H | 8 | 2·47 | 2·54 |
| 2 Br | 160 | 49·38 | 49·17 |
| 6 O | 48 | 14·82 | 14·95 |
| $C^{18}H^8Br^2O^6$ | 324 | 100·00 | 100·00 |

By continued contact with ammonia, it forms an amide containing bromine.

It dissolves in strong potash-ley and is precipitated therefrom in its original state by acids.

## Sulphide of Hydrogen and Bibromosalicene.

$C^{14}Br^2H^6O^2S^4 = C^{14}Br^2H^4O^2,S^2 + 2HS$.

HEERLEIN. (1838.) *J. pr. Chem.* 32, 68.

When sulphuretted hydrogen is passed for some hours through an alcoholic solution of bibromosalicylous acid mixed with a little ammonia, and water then added, a brown, resinous mass is precipitated; and when this is dissolved in alcohol and the solution evaporated, a brown-red body remains which does not dissolve completely in ether. The ethereal solution is mixed with alcohol, precipitated by water, and the precipitate dried at 100°. The compound resembles the sulphide of bromosalicene.

| | | | Heerlein. |
|---|---|---|---|
| 14 C | 84 | 25·45 | 25·09 |
| 2 Br | 160 | 48·49 | 47·02 |
| 6 H | 6 | 1·82 | 1·90 |
| 2 O | 16 | 4·85 | 6·73 |
| 4 S | 64 | 19·39 | 19·30 |
| $C^{14}Br^2H^6O^2S^4$ | 330 | 100·00 | 100·00 |

*Oxybromine-nucleus* $C^{14}BrH^3O^2$.

## Terbromosalicylic Acid.

$C^{14}Br^3H^3O^6 = C^{14}Br^3H^3O^2,O^4$.

CAHOURS. (1845.) *Ann. Chim. Phys.* 13, 104; *Ann. Pharm.* 52, 339; *J. pr. Chem.* 35, 84; *Pharm. Centr.* 1845, 885.

*Formation and Preparation.* A mixture of finely pulverised bibromosalicylic acid with excess of bromine is exposed to sunshine for 25 or 30 days, and the resulting yellowish crystals washed with water and recrystallised from strong alcohol.

*Properties.* Small yellowish prisms, very hard and friable.

| | | | Cahours. |
|---|---|---|---|
| 14 C | 84 | 22·40 | 24·05 |
| 3 Br | 240 | 64·00 | 63·72 |
| 3 H | 3 | 0·80 | 1·23 |
| 6 O | 48 | 12·80 | 11·00 |
| $C^{14}Br^3H^3O^6$ | 375 | 100·00 | 100·00 |

*Decompositions.* When distilled with sand and a small quantity of baryta, it yields terbromocarbolic acid contaminated with a small quantity of oily matter.

When boiled with nitric acid, it yields bromine-vapours and yellow crystals.

It is insoluble in water. — Its compounds with ammonia, potash and soda are crystallisable, but very sparingly soluble in water. The ammonia-salt forms with silver-salts a precipitate of a deep orange-yellow colour.

It dissolves with tolerable facility in *alcohol*, very readily in *ether*.

*Chlorine-nucleus* $C^{14}ClH^7$.

## Chlorotoluol.

$C^{14}ClO^7$.

DEVILLE. *N. Ann. Chim. Phys.* 3, 178. — *J. pr. Chem.* 25, 336; abstr. *J. Pharm.* 27, 640.

*Benzoène monochloré, Chlorobenzoénase.*

Toluol is saturated in the dark with chlorine gas (p. 229); the excess of chlorine expelled from the liquid by a stream of carbonic acid gas at a temperature between 50° and 60°; and the liquid distilled till hydrochloric acid begins to escape. The distillate is purified by repeated distillation.

Colourless, very thin oil. Boils without decomposition at 170°.

| | | | | Deville. |
|---|---|---|---|---|
| 14 C | 84·0 | 66·45 | | 66·12 |
| Cl | 35·4 | 28·01 | | |
| 7 H | 7·0 | 5·54 | | 6·13 |
| $C^{14}ClH^7$ | 126·0 | 100·00 | | |

*Chlorine-nucleus* $C^{14}Cl^3H^5$.

## Hydrochlorate of Terchlorotoluol.

$C^{14}Cl^4H^8 = C^{14}Cl^3H^5,HCl$(or $C^{14}Cl^3H^6,Cl^2$ ?).

DEVILLE. *N. Ann. Pharm.* 3, 178 ; *J. pr. Chem.* 25, 336 ; abstr. *J. Pharm.* 27, 640.

*Chlorhydrate de chlorobenzoénise.*

Chlorine gas is passed through toluol in bright daylight, as long as hydrochloric acid continues to form, and the liquid is purified by a stream of carbonic acid.

| | | | | Deville. |
|---|---|---|---|---|
| 14 C | 84·0 | 36·30 | | 35·45 |
| 4 Cl | 141·4 | 61·10 | | |
| 6 H | 6·0 | 2·60 | | 2·65 |
| $C^{14}H^4Cl^6$ | 231·4 | 100·00 | | |

When distilled it decomposes and gives off hydrochloric acid.

*Chlorine-nucleus* $C^{14}Cl^5H^3$.

## Bihydrochlorate of Quintichlorotoluol.

$C^{14}Cl^7H^5 = C^{14}Cl^5H^3,2HCl$(or $C^{14}Cl^3H^5,Cl^4$ ?).

DEVILLE. *loc. cit.*

*Bihydrochlorate de chlorobenzoénise.*

When chlorine gas is passed for a considerable time by daylight through toluol, a thickish liquid is produced in which crystals separate. The liquid is separated from the crystals, still further treated by chlorine with the aid of heat, and purified by a stream of carbonic acid. When distilled it gives of hydrochloric acid.

| | | | | Deville. |
|---|---|---|---|---|
| 14 C | 84·0 | 24·94 | | 24·74 |
| 7 Cl | 247·8 | 73·57 | | |
| 5 H | 5·0 | 1·49 | | 1·63 |
| $C^{14}Cl^7H^3$ | 336·8 | 100·00 | | |

In Deville's memoir, the formula assigned to this compound is $C^{14}Cl^5H^7$ (probably a misprint), whence Gerhardt deduces the formula $C^{14}H^7Cl,2Cl^2$ (*Traité*, 3, 566). L.

The compound is soluble in *ether*.

## Terhydrochlorate of Quintichlorotoluol.

DEVILLE. *loc. cit.*

Produced by the action of chlorine on toluol in daylight, and with peculiar rapidity in sunshine, together with bihydrochlorate of quintichlorotoluol, from which it separates in crystals. These are purified by recrystallisation from ether, but are difficult to free completely from the adhering oil.

Colourless transparent crystals.

| | | | Deville. |
|---|---|---|---|
| 14 C | 84·0 | 22·50 | 22·63 |
| 8 Cl | 283·2 | 75·88 | 75·55 |
| 6 H | 6·0 | 1·62 | 1·82 |
| $C^{14}Cl^{8}H^{6}$ | 373·2 | 100·00 | 100·00 |

It is soluble in *ether*, especially when heated or under somewhat increased pressure.

*Chlorine-nucleus* $C^{14}Cl^{6}H^{2}$.

## Sexichlorotoluol.

$C^{14}H^{6}Cl^{2}$.

DEVILLE. *loc. cit.*

*Benzoène sexchloré, Chlorobenzoènyle.*

When the mixture of bihydrochlorate and terhydrochlorate of quintichlorotoluol is distilled in a stream of chlorine gas, and cohobated 10 or 12 times, a small quantity of a substance having a silky lustre condenses in the receiver at the end of each distillation, and at length the entire liquid is converted into this substance. A large quantity of hydrochloric acid is evolved at the same time. By pressure between paper and recrystallisation from ether, the silky substance is obtained quite pure. It may be volatilised without decomposition.

| | | | Deville. |
|---|---|---|---|
| 14 C | 84·0 | 28·15 | 27·6 |
| 6 Cl | 212·4 | 71·18 | 71·7 |
| 2 H | 2·0 | 0·67 | 0·7 |
| $C^{14}Cl^{6}H^{2}$ | 298·4 | 100·00 | 100·0 |

*Oxychlorine-nucleus* $C^{14}ClH^{5}O^{2}$.

## Chlorosaligenin.

$C^{14}ClH^{7}O^{4} = C^{14}ClH^{5}O^{2},2HO$.

PIRIA. *N. Ann. Chim. Phys.* 14, 284.—*Ann. Pharm.* 56, 60.

Chlorosalicin is treated with emulsin in the same manner as salicin in the preparation of saligenin (p. 233).

Crystallises from hot water in beautiful colourless rhombic tables which in external appearance are undistinguishable from saligenin.

| | | | Piria. |
|---|---|---|---|
| 14 C | 84·0 | 53·16 | 52·75 |
| 7 H | 7·0 | 4·43 | 4·64 |
| Cl | 35·4 | 22·15 | 22·34 |
| 4 O | 32·0 | 20·26 | 20·27 |
| $C^{14}ClH^7O^4$ | 158·4 | 100·00 | 100·00 |

Acids convert it into a resin.

With oil of vitriol it assumes a bright green colour. It colours ferric salts blue.

Soluble in *water, alcohol* and *ether*.

## Chloride of Salicyl.

$C^{14}ClH^5O^4 = C^{14}ClH^5,O^4$

GERHARDT. *Compt. rend.* 38, 34; *Ann. Pharm.* 89, 363.—*Traité*, 3, 344

*Chlorsalicyl, Salicylchlorür.*

*Formation* (p. 256).

*Preparation.* The product of the action of pentachloride of phosphorus on methylsalicylic acid, forms, after a small quantity of chlorophosphoric acid has been expelled by heating to about 160°, a fuming, slightly coloured liquid, which cannot be distilled without decomposition, but deposits a large quantity of charcoal, gives off hydrochloric acid, and yields a liquid which appears to be the compound regarded by Chiozza as $C^{14}H^5ClO^2,HCl$ (p. 113), and by Gerhardt as chloride of chlorobenzoyl ($C^{14}ClH^5O^2,Cl$). It probably also contains phosphate of salicyl (p. 256). With water, it becomes heated and yields hydrochloric and salicylic acids. With wood-spirit or alcohol, it forms methylsalicylic or ethylsalicylic acid and hydrochloric acid.

## Chlorosalicylous Acid.

$C^{14}ClH^5O^4 = C^{14}ClH^5O^2,O^2$.

PAGENSTECHER. *Repert.* 49, 341; *Ann. Chim. Phys.* 69, 334.
LÖWIG. *Pogg* 36, 398.
DUMAS. *Ann. Chim. Phys.* 69, 326; *Ann. Pharm.* 29, 306; *Pharm. Centr.* 1839, 375.
PIRIA. *Ann. Pharm.* 30, 169; *Pharm. Centr.* 1839, 375.
LÖWIG & WEIDMANN. *Pogg.* 46, 63; *Pharm. Centr.* 1839, 130.
ETTLING. *Ann. Pharm.* 35, 245.
BERTAGNINI. *Ann. Pharm.* 85, 196.

*Chlorsalicyl, Chlorspiroyl, chlorspiroylige Säure, chlorspirige Säure.*

*Preparation.* When dry chlorine gas is passed at ordinary temperatures into dry salicylous acid, the liquid becomes hot, assumes a yellow

colour, gives off hydrochloric acid, and solidifies on cooling into a crystalline mass, which may be recrystallised from hot alcohol. (Dumas, Piria, Ettling), or sublimed at a gentle heat. (Löwig.)

*Properties.* Beautiful crystalline laminæ of a dazzling whiteness. (Löwig.) Colourless rectangular tables having a pearly lustre. Melts below 100°, forming a colourless liquid, and then evaporates, subliming in long needles. Boils at a temperature not much below 100°, and sublimes without decomposition together with the watery vapours. (Löwig.) Has a peculiar aromatic odour, somewhat like that of dilute hydrocyanic acid (Löwig); has a peculiar disagreeable odour and a peppery taste. (Piria.)

| | | | Dumas. | Piria. | Löwig & Weidmann. |
|---|---|---|---|---|---|
| 14 C | 84·0 | 53·69 | 53·48 | 53·91 | 52·77 |
| 5 H | 5·0 | 3·19 | 3·28 | 3·30 | 3·66 |
| Cl | 35·4 | 22·63 | | 22·32 | 24·10 |
| 4 O | 32·0 | 20·49 | | 20·47 | 19·47 |
| $C^{14}ClH^5O^4$ | 156·4 | 100·00 | | 100·00 | 100·00 |

*Decompositions.* 1. The vapour may be set on fire and *burns* with a green-edged flame. (Piria, Löwig.) — 2. By the action of *chorine* it is converted into bichlorosalicylous acid. (Löwig & Weidmann.) — 3. It absorbs *ammoniacal gas*, acquiring a yellow colour, and forming a resinous mass of chlorosalicylimide, while water escapes. (Piria.) — 4. After boiling with excess of potash-ley, it is precipitated in its original state by acids. (Piria, Löwig.) — 5. When fused at a gentle heat with potassium it exhibits vivid combustion, part of the acid being decomposed and charcoal separated, while the rest combines with potash produced in the reaction. On dissolving the residue in water and adding nitric acid, chlorosalicylous acid is precipitated, and the liquid retains a large quantity of hydrochloric acid. (Löwig.)

*Combinations.* 1. The acid is insoluble in water. — 2. It dissolves in cold oil of vitriol and is precipitated without alteration by water. — 3. With bases it forms yellow salts. The chlorosalicylites of the alkalis are less soluble in water [than the salicylites ?]; the solutions impart a black-blue colour to ferric salts. (Pagenstecher, Löwig.)

*Chlorosalicylite of Potash.* — When hot aqueous potash of 45° Bm. is saturated with chlorosalicylous acid, the deep yellow solution deposits the salt in red scales united in radiated groups. (Piria.) — Insoluble in alcohol. When heated, it exhibits incandescence long before the containing vessel attains a red heat. (Löwig.)

*Chlorosalicylite of Baryta.* — Obtained by decomposing chlorosalicylite of potash or ammonia with chloride of barium. Yellow crystalline powder. (Piria, Löwig.)

| | | | Löwig & Weidmann. |
|---|---|---|---|
| BaO | 76·6 | 34·19 | 33·01 |
| $C^{14}ClH^4O^3$ | 147·4 | 65·81 | |
| $C^{14}ClH^4BaO^4$ | 224·0 | 100·00 | |

Piria found 31·92 p. c. baryta and 14·98 chlorine, agreeing nearly with the formula $C^{14}ClH^4BaO^4$ + 2Aq which requires 31·65 baryta and 14·63 chlorine.

When chlorosalicylous acid is boiled with excess of baryta-water and the excess of baryta removed by carbonic acid, the liquid deposits small silvery laminæ consisting of a compound of 3 At. bicarbonate of baryta with 1 At. acid chlorosalisalicylite of baryta. (Löwig & Weidmann.) [Instead of this improbable composition, we may substitute the formula $(BaO,CO^2 + HO,CO^2) + C^{14}ClH^4BaO^4 + Aq$. (L.)]

| | | | |
|---|---|---|---|
| 2 BaO | 153·2 | | 42·25 |
| 16 C | 96·0 | | 26·47 |
| 6 H | 6·0 | | 1·65 |
| Cl | 35·4 | | 9·76 |
| 9 O | 72·0 | | 19·87 |
| $(BaO,CO^2 + HO,CO^2) + C^{14}ClH^4BaO^4 + Aq$ | 362·6 | | 100·00 |

| | | | | Löwig & Weidmann. |
|---|---|---|---|---|
| 4 BaO | 306·4 | | 39·83 | 41·66 |
| 34 C | 204·0 | | 26·52 | 25·71 |
| 12 H | 12·0 | | 1·56 | 1·60 |
| 2 Cl | 70·8 | | 9·20 | 9·45 |
| 22 O | 176·0 | | 22·89 | 21·58 |
| $3(BaO,HO,2CO^2) + C^{14}ClH^4BaO^4 + C^{14}ClH^5O^4$ | 769·2 | | 100·00 | 100·00 |

Chlorosalicylous acid dissolves readily in aqueous bisulphite of ammonia or potash; the solution formed with the aid of heat, deposits the resulting compound in the crystalline form on cooling. (Bertagnini.)

The alcoholic solution of the acid forms a yellow precipitate with *lead-salts*, and greenish yellow with acetate of copper. (Pagenstecher, Löwig.)

The acid dissolves readily in *alcohol* and *ether*.

## Chlorosalicylic Acid.

$C^{14}ClH^5O^6 = C^{14}H^5ClO^2,O^4$.

CAHOURS. (1845.) *N. Ann. Chim. Phys.* 13, 106.

*Acide monochlorosalicylique.*

*Formation and Preparation.* 1. By the action of chlorine on excess of salicylic acid, a portion of the acid therefore remaining undecomposed; it is difficult however to purify from bichlorosalicylic acid. — 2. Chlorine gas is very slowly passed into a concentrated solution of salicylate of potash, till the liquid, which becomes brown, begins to deposit a dark green substance; the solution is then decomposed by an acid, and the resulting white precipitate washed with water. By crystallisation from alcohol, slender needles are obtained, consisting of chlorosalicylic acid not quite pure.

## Methylchlorosalicylic Acid.

$C^{16}ClH^7O^6 = C^2H^3O,C^{14}ClH^4O^5$.

CAHOURS. (1844.) *N. Ann. Chim. Phys.* 10, 343; *Pharm. Centr.* 1844, 438.

*Salicylate de methylène monochloré, Chlorsalicylformester.*

When methylsalicylic acid is exposed to the action of a small quantity of chlorine, methylchlorosalicylic acid is formed, with rise of temperature and evolution of hydrochloric acid, but is difficult to purify.

*Oxychlorine-nucleus* $C^{14}Cl^2H^4O^2$.

## Bichlorosaligenin.

$C^{14}Cl^2H^6O^4 = C^{14}Cl^2H^4O^2,2HO$.

PIRIA. *N. Ann. Chim. Phys.* 14, 285; *Ann. Pharm.* 56, 60.

Produced in very small quantity, when bichlorosalicin is treated with emulsin in the same manner as salicin for the preparation of saligenin (p. 233).

## Bichlorosalicylous Acid.

$C^{14}ClH^5O^4 = C^{14}ClH^5O^3,O^2$.

LÖWIG & WEIDMANN. *Pogg.* 46, 63; *Pharm. Centr.* 1839, 130.

Salicylous or chlorosalicylous acid treated with excess of chlorine-water first turns yellow, then red, and ultimately black, the water also acquiring a reddish colour. As soon as the action is finished, the excess of chlorine is removed by adding a few drops of ammonia; the whole is shaken up with ether; and the ethereal solution is left to evaporate. Crystals of chlorosalicylous acid are then deposited, and the mother-liquor yields bichlorosalicylous acid, which when freed as completely as possible from chlorosalicylous acid by repeated solution in ether and alcohol, forms a red, thick, oily liquid, becoming perfectly fluid at 25°; it has a pungent odour and excites tears.

| | | | Löwig & Weidmann. |
|---|---|---|---|
| 14 C | 84·0 | 44·02 | 39·84 |
| 4 H | 4·0 | 2·09 | 2·39 |
| 2 Cl | 70·8 | 37·11 | 37·06 |
| 4 O | 32·0 | 16·78 | 20·71 |
| $C^{14}Cl^2H^4O^4$ | 190·8 | 100·00 | 100·00 |

Sparingly soluble in water. Dissolves with deep red colour in potash-ley. With baryta it forms a ruby-coloured compound sparingly soluble in water.

The acid dissolves readily in *alcohol* and *ether*. (Löwig & Weidmann.)

## Bichlorosalicylic Acid.

$C^{14}Cl^2H^4O^6 = C^{14}Cl^2H^4O^2,O^2$.

CAHOURS. (1845.) *N. Ann. Chim. Phys.* 13, 106; *Pharm. Centr.* 1845, 885.

Produced by the action of excess of chlorine on salicylic acid.

Chlorine gas is passed through a concentrated solution of salicylate of potash, till the liquid which has become brown ceases to deposit a dark green body; this substance is washed on a filter with water till the water runs away colourless, then dissolved in boiling water which is mixed with $\frac{1}{8}$ of its volume of alcohol of 36° Bm.; and the needles of the potash-salt which separate on cooling, are repeatedly crystallised from very weak spirit till they become colourless. These crystals are then dissolved in water; the solution mixed with hydrochloric acid; and the resulting white precipitate dissolved in boiling alcohol of 82 per cent.: the solution on cooling yields the acid in needles or in scales, or by spontaneous evaporation, in hard, well formed octohedrons.

| | | | Cahours. |
|---|---|---|---|
| 14 C | 84·0 | 40·62 | 40·76 |
| 2 Cl | 70·8 | 34·24 | 34·22 |
| 4 H | 4·0 | 1·93 | 2·09 |
| 6 O | 48·0 | 23·21 | 22·93 |
| $C^{14}Cl^2H^4O^6$ | 206·8 | 100·00 | 100·00 |

The acid distilled two or three times with sand and a small quantity of baryta or lime, is completely resolved into carbonic and bichlorocarbolic acids. It dissolves gradually in boiling nitric acid and deposits beautiful yellow laminæ on cooling.

*Combinations.* The acid dissolves sparingly in boiling *water* and crystallises in slender needles on cooling. It dissolves in gently heated *oil of vitriol*, and separates partially as the liquid cools.

*Bichlorosalicylate of Ammonia* is sparingly soluble in water.

*Acid Bichlorosalicyate of Potash.* — Greyish white needles very much resembling methylbichlorosalicylic acid.

| | | | Cahours. |
|---|---|---|---|
| KO | 47·2 | 19·27 | 19·24 |
| 14 C | 84·0 | 34·29 | |
| 2 Cl | 70·8 | 28·90 | 28·39 |
| 3 H | 3·0 | 1·21 | |
| 5 O | 40·0 | 16·33 | |
| $C^{14}Cl^2H^3KO^6$ | 245·0 | 100·00 | |

The acid forms reddish precipitates with *lead* and *silver* salts.

It dissolves very readily in *alcohol*, still more in *ether*.

## Methylbichlorosalicylic Acid.

$C^{16}Cl^2H^6O^6 = C^2H^3O,C^{14}Cl^2H^3O^5$.

PROCTER. (1843.) *N. J. Pharm.* 3, 275; *J. pr. Chem.* 29, 467; *Ann. Pharm.* 48, 66.
CAHOURS. *N. Ann. Chim. Phys.* 10, 343.

*Bichlorsalicylformester.*

When chlorine gas is passed into methylsalicylic acid till the action ceases, a yellowish crystalline mass is formed, consisting of methylbichlorosalicylic acid mixed with a small quantity of liquid methylchlorosalicylic acid. By crystallisation from boiling alcohol, the bichlorinated acid is obtained in colourless rhombic tables (Procter), in needles (Cahours). Melts at 104° (Procter), at about 100° (Cahours), and crystallises on cooling. Volatilises without decomposition at a stronger heat (Cahours), and sublimes a little above its melting point in rhombic crystals.

| | | | Cahours. |
|---|---|---|---|
| 16 C | 96·0 | 43·48 | 43·41 |
| 2 Cl | 70·8 | 32·06 | 32·15 |
| 6 H | 6·0 | 2·72 | 2·98 |
| 6 O | 48·0 | 21·74 | 21·46 |
| $C^{16}Cl^2H^6O^6$ | 220·8 | 100·00 | 100·00 |

The acid burns with a yellowish flame.

It dissolves slowly in ammonia, forming a chlorinated amide. (Cahours.) When ammoniacal gas is passed over the acid for several hours, it turns grey. The product washed with water,—which then becomes yellowish and precipitates a solution of silver,—and afterwards dried and dissolved in hot alcohol, crystallises on cooling in yellow laminæ which dissolve in potash without evolution of ammonia. Acids precipitate from the solution a white substance which appears to be chlorososalicylimide. (Procter.)

The acid is not altered by chlorine in sunshine When distilled with cyanide of mercury, it yields a compound in which the chlorine is replaced by cyanogen.

It is insoluble in water. It dissolves without decomposition in cold *potash-ley*, and may be reprecipitated by acids.

It dissolves in *alcohol* and *ether*.

## Ethylbichlorosalicylic Acid.

$C^{18}Cl^2H^8O^6 = C^4H^5O,C^{14}Cl^2H^3O^5$.

CAHOURS. (1849.) *N. Ann. Chim. Phys.* 27, 461; *Ann. Pharm.* 74, 313; *J. pr. Chem.* 49, 231.

*Bichlorosalicylvinester.*

Ethylsalicylic acid heated in the water-bath is saturated with chlorine gas, the product ultimately solidifying, and the solid mass is pressed between paper and twice crystallised from alcohol.

Colourless plates having a strong lustre.

| | | | Cahours. |
|---|---|---|---|
| 18 C | 108·0 | 45·95 | 45·72 |
| 2 Cl | 70·8 | 30·21 | 30·41 |
| 8 H | 8·0 | 3·41 | 3·44 |
| 6 O | 48·0 | 20·43 | 20·43 |
| $C^{18}Cl^{2}H^{8}O^{6}$ | 234·8 | 100·00 | 100·00 |

*Nitro-nucleus* $C^{14}XH^{7}$.

## Nitrotoluol.

$C^{14}NH^{7}O^{4} = C^{14}XH^{7}$.

DEVILLE. (1841.) *N. Ann. Chim. Phys.* 3, 170; *J. pr. Chem.* 25, 341; *Pharm. Centr.* 1842, 198.
GLÉNARD & BOUDAULT. *N. J. Pharm.* 6, 250; *Compt. rend.* 19, 505; *J. pr. Chem.* 33, 459; *Pharm. Centr.* 1844, 156.
MUSPRATT & HOFMANN. *Ann. Pharm.* 53, 221 and 224.

*Nitrotoluene, Pronitrobenzoene, Nitrobenzoenase, Nitrodracyl, Nitrotoluide, Nitrotole.*

*Preparation.* Toluol is poured by drops into fuming nitric acid which is kept cool, the addition of the toluol being continued as long as it dissolves immediately (Deville), or fuming nitric acid is poured into toluol till the latter is completely dissolved (Glénard & Boudault), and the clear red liquid is mixed with a large quantity of water, which separates the nitrotoluol in the form of a red liquid; it may be decolorised by washing with water and repeated distillation.

*Properties.* Nearly colourless liquid (Deville); amber-coloured (Glénard & Boudault.) Sp. gr. 1·180 at 16·5°. (Deville.) Smells like bitter almonds (Deville) and benzol (Glénard & Boudault.) Its taste is very sweet, with a somewhat pungent aftertaste. Boils at 225° (Deville); at 230° (E. Kopp, *Compt. chim.* 1849, 149); at 220° to 225° (Wilson, *Ann. Pharm.* 77, 216). Vapour-density = 4·95.

| | | | Deville. |
|---|---|---|---|
| 14 C | 84 | 61·31 | 61·18 |
| 7 H | 7 | 5·11 | 5·26 |
| N | 14 | 10·22 | 10·75 |
| 4 O | 32 | 23·36 | 22·81 |
| $C^{14}NH^{7}O^{4}$ | 137 | 100·00 | 100·00 |

Isomeric with benzamic, anthranilic, and salicylamic acids.

*Decompositions* 1. Each time it is distilled, it leaves a residue, and yields a distillate containing more carbon and less nitrogen than the preceding; hence it must only be distilled with water and dried over chloride of calcium. (Glénard & Boudault.) The vapours passed

through a red-hot tube filled with pieces of glass, remain undecomposed at a moderate heat; but a stronger heat decomposes them, producing a deposit of black soot. (Muspratt & Hofmann.) — 2. The compound burns with a sooty flame, emitting the odour of gum benzoïn. — 3. It dissolves with decomposition in aqueous *potash*, forming a red solution (Deville), more quickly in alcoholic potash, forming a black liquid. (Ritthausen, *J. pr. Chem.* 61, 114.) Hydrochloric acid added to the potash-solution throws down a brown powder. When the solution in alcoholic potash is distilled, there passes over, after the alcohol, a reddish oil, probably analogous to azobenzide (Deville), containing aniline and azobenzoene. (Muspratt & Hofmann.) — 4. The vapour passed over *red-hot baryta* is resolved into aniline and carbonic acid. (Muspratt & Hofmann):

$$C^{14}NH^7O^4 = C^{12}NH^7 + 2CO^2.$$

5. With fuming sulphuric acid it forms nitrosulphotoluic acid $C^{14}XH^7S^2O^6$. (Church, *Phil. Mag.* [4], 9, 256.) — 6. By boiling with an alcoholic solution of sulphite of ammonia, it is converted into the ammonia-salt of thiotoluic acid, $C^{14}NH^4S^2O^6$. (Hilkenkamp, *Ann. Pharm.* 95, 86.) — 7. With hydrosulphate of ammonia it yields toluidine.

It dissolves with great facility in *alcohol* and *ether*.

*Nitro-nucleus* $C^{14}X^2H^6$.

## Binitrotoluol.

$$C^{14}N^2H^6O^6 = C^{14}X^2H^6.$$

DEVILLE. *N. Ann. Chim. Phys.* 3, 175; *J. pr. Chem.* 25, 341; *Pharm. Centr.* 1842, 199.
CAHOURS. *Compt rend.* 24. 555.

*Binitrotoluene, Binitrobenzoene, Nitrobenzoenèse.*

Produced by boiling toluol for a considerable time with fuming nitric acid (Deville) or by treating it with nitrosulphuric acid. (Cahours.)

Crystallises from alcohol in long needles having a strong lustre, and in prisms belonging to the right prismatic system. Melts at 71°, and solidifies in a radiated mass on cooling. Very hard and brittle. When strongly heated, it gives off vapours which form a sublimate on the neighbouring part of the vessel. Boils at 300°, becoming coloured and leaving a considerable residue.

| | | | Deville. |
|---|---|---|---|
| 14 C | 84 | 46·16 | 46·1 |
| 2 N | 28 | 15·39 | 15·5 |
| 6 H | 6 | 3·30 | 3·5 |
| 8 O | 64 | 35·15 | 34·9 |
| $C^{14}N^2H^6O^6$ | 182 | 100·00 | 100·0 |

Its solution in potash yields a red-brown powder on the addition of hydrochloric acid. (Deville.)

With hydrosulphate of ammonia it forms nitrotoluidine. (Cahours.)

It dissolves but sparingly in water, even when accidulated with nitric acid.

*Nitro-nucleus* $C^{14}X^3H^5$.

## Chrysanisic Acid.

$C^{14}N^3H^5O^{14} = C^{14}X^3H^5,O^2$.

CAHOURS. (1849.) *Compt. rend.* 28, 385; *N. Ann. Chim. Phys.* 27, 454; *J. pr. Chem.* 49, 274; *Pharm. Centr.* 1849, 309.

*Formation.* By the action of fuming nitric acid on anisic acid, binitranisol and ternitranisol being formed at the same time.

*Preparation.* When 1 pt. of perfectly dry anisic acid is very gently boiled, for half or three-quarters of an hour, with 2½ pts. of fuming nitric acid, and the somewhat thick liquid is mixed with 20 times its bulk of water, a yellow oil separates out, which soon coagulates into a solid mass consisting of chrysanisic acid mixed with bi- and ter-nitranisol. This mixture, in the form of fine powder, is washed on a filter with ammonia diluted with two or three times its bulk of water, whereby the acid is extracted; the ammoniacal liquid, after being evaporated to one-third, yields on cooling brown needles of the ammonia-salt. These crystals are dissolved in water; the solution mixed with dilute hydrochloric acid; the separated yellow flakes are collected on a filter, repeatedly washed with cold water, dried between bibulous paper, and dissolved in hot alcohol; and the scales which crystallise from the solution on cooling, are dried.

Small golden-yellow rhombic tables. The acid melts when cautiously heated and solidifies in the crystalline form on cooling; at a stronger heat, it emits a yellow vapour which condenses in small crystalline scales having a strong lustre.

| | | | Cahours. |
|---|---|---|---|
| 14 C | 84 | 34·57 | 34·54 |
| 3 N | 42 | 17·28 | 17·48 |
| 5 H | 5 | 2·06 | 2·00 |
| 14 O | 112 | 46·09 | 45·98 |
| $C^{14}N^3H^5O^{14}$ | 243 | 100·00 | 100·00 |

Isomeric with ternitranisol.

*Decompositions.* 1. When boiled with strong nitric acid, it is converted into picric acid. — 2. Distilled with aqueous chloride of lime, it yields chloropicrin. — 3. By boiling with potash, it is converted into a brown substance.

*Combinations.* It is not perceptibly soluble in cold water, and dissolves but sparingly in hot water, crystallising as it cools.

*Chrysanisate of Ammonia.* — The solution of the acid in dilute ammonia, evaporated over the water-bath, yields on cooling, small brown needles having a strong lustre. Finer crystals are obtained by spontaneous evaporation of the solution.

| | | | | Cahours. |
|---|---|---|---|---|
| 14 C | 84 | 32·32 | | 32·72 |
| 4 N | 56 | 21·54 | | 21·29 |
| 8 H | 8 | 3·08 | | 3·14 |
| 14 O | 112 | 43·06 | | 42·85 |
| $C^{14}N^3H^4(NH^4)O^{14}$ | 260 | 100·00 | | 100·00 |

*Chrysanisate of Potash.* — Obtained by exactly saturating the acid with potash. Very easily soluble.

The ammonia-salt produces in solutions of zinc-salts a pale yellow precipitate; with nitrate of *cobalt*, a greenish yellow gelatinous precipitate; with nitrate of *lead*, a copious deposit of chrome-yellow flakes; with *ferric* salts a pale yellow, with *cupric* salts a greenish yellow, gelatinous precipitate; and with *mercuric* chloride, yellowish red flakes, which in dilute solutions appear after a time only.

*Chrysanisate of Silver.* — The ammonia-salt forms with nitrate of silver, beautiful yellow flakes, which must be washed with water and dried in vacuo.

| | | | | Cahours. |
|---|---|---|---|---|
| 14 C | 84 | 24·10 | | 23·97 |
| 3 N | 42 | 12·00 | | |
| 4 H | 4 | 1·14 | | 1·20 |
| Ag | 108 | 30·85 | | 30·90 |
| 14 O | 112 | 31·91 | | |
| $C^{14}N^3H^4AgO^{14}$ | 350 | 100·00 | | |

Chrysanisic acid dissolves but very sparingly in cold *alcohol*, but so abundantly in hot alcohol that the liquid solidifies on cooling. It dissolves in *ether* especially if hot, and crystallises in shining laminæ when the solution evaporates.

## Chrysanisate of Ethyl.

$$C^{18}N^3H^9O^{14} = C^4H^5O,C^{14}X^3H^4O.$$

The alcoholic solution of the acid is saturated with dry hydrochloric acid gas, gently boiled for some time and then mixed with water; the resulting precipitate is washed, first with ammoniacal, afterwards with pure water, then dissolved in boiling alcohol; and the solution is left to cool.

Transparent crystalline laminæ of a splendid golden yellow colour. Melts at about 100°.

| | | | | Cahours. |
|---|---|---|---|---|
| 18 C | 108 | 39·85 | | 39·65 |
| 3 N | 42 | 15·49 | | 15·27 |
| 9 H | 9 | 3·32 | | 3·33 |
| 14 O | 112 | 41·34 | | 41·75 |
| $C^{18}N^3H^9O^{14}$ | 271 | 100·00 | | 100·00 |

Soluble in warm *ether*.

*Oxynitro-nucleus* $C^{14}XH^5O^2$.

## Nitrosalicylous Acid.

$C^{14}NH^5O^8 = C^{14}XH^5O^2,O^2$.

PAGENSTECHER. (1834.) *Repert.* 49, 337; *Ann. Chim. Phys.* 69, 331; *Pharm. Centr.* 1835, 137.
LÖWIG. *Pogg.* 36, 394; *Pharm. Centr.* 1836, 61.
LÖWIG & WEIDMANN. *Pogg.* 46, 57; *Pharm. Centr.* 1839, 131.
HEERLEIN. *J. pr. Chem.* 32, 70; *Pharm. Centr.* 1844, 600.
BERTAGNINI. *Ann. Pharm.* 85, 196.

***Nitrosalicide, Nitrospiroylic acid, Nitrospiroilsäure, Spirräasalpetersäure, Spiroylsäure*** (Löwig).

*Formation and Preparation.* Salicylous acid is heated with moderately strong nitric acid not in excess, and the crystalline mass which separates on cooling is recrystallised from alcohol.

*Properties.* Golden yellow transparent needles. Nearly inodorous; tastes but slightly at first, but afterwards produces irritation in the throat and coughing. Melts when heated and solidifies in the crystalline state on cooling; at a high temperature it sublimes partly undecomposed, leaving a small quantity of charcoal. Colours litmus paper deep yellow, not red. The solutions produce a permanent yellow stain on the skin and nails.

| | | | Löwig. | Löwig & Weidmann. |
|---|---|---|---|---|
| 14 C | 84 | 50·73 | 51·05 | 49·16 |
| N | 14 | 8·39 | | 8·43 |
| 5 H | 5 | 2·96 | 3·46 | 3·42 |
| 8 O | 64 | 37·92 | | 38·99 |
| $C^{14}NH^5O^8$ | 167 | 100·00 | | 100 00 |

Isomeric with nitrobenzoic acid.

*Decomposition.* 1. Heated for some time with nitric acid, it forms picric acid. — 2. Potassium very slightly heated with the acid over mercury, decomposes it with the most vivid combustion, attended with destruction of the vessel, the product being a mixture of carbonate and salicylite [? L.] of potash. (Löwig.) — 3. The alcoholic solution saturated with ammonia and sulphuretted hydrogen, acquires a dark brown-red colour; water precipitates from it only a few flakes; but hydrochloric acid throws down a copious red-brown, resinous precipitate, which, after being several times dissolved in alcohol and ether, and then dried over the water-bath, contains 33 or 34 per cent. of sulphur. (Heerlein.)

*Combinations.* The acid absorbs moisture from the air, acquiring thereby a deep yellow colour. It dissolves but sparingly in water.

It dissolves abundantly, with the aid of heat, in aqueous bisulphite of ammonia, potash or soda. The compound with bisulphite of ammonia does not appear to crystallise; the compound with bisulphite of soda

separates on cooling from a warm solution, in aggregated golden-yellow needles, which are soluble in water, but insoluble in alcohol. The potash-compound appears to be more soluble. (Bertagnini.)

The *nitrosalicylites* are yellow or yellowish red. They detonate violently when heated, leaving a residue of oxide or carbonate.

*Nitrosalicylite of Ammonia.* — The acid dissolves abundantly in ammonia. The dark blood-red solution leaves when evaporated a dark yellow residue, which immediately gives off ammonia when treated with potash (Pagenstecher, Löwig), and when heated in close vessels, yields a small quantity of ammonia and an oily distillate. (Löwig.)

The *fixed alkalis* combine readily with the acid, forming dark yellow solutions, which, when evaporated, leave small crystals soluble in alcohol but insoluble in ether. (Löwig.) The *soda-salt* yields by evaporation, delicate saffron-coloured needles having a silky lustre.

*Nitrosalicylite of Baryta.* — By dissolving the acid in baryta-water, precipitating the excess of baryta by carbonic acid, and evaporating the reddish yellow filtrate, this salt is obtained in reddish yellow crystalline laminæ, soluble in water.

| | *At* 100°. | | Löwig & Weidmann. |
|---|---|---|---|
| BaO | 76·6 | 31·32 | 32·9 |
| $C^{14}NH^4O^7$ | 168·0 | 68·68 | |
| $C^{14}NH^4BaO^8$ | 244·6 | 100·00 | |

*Nitrosalicylite of Lead.* — Neutral acetate of lead mixed with the baryta-salt forms a dark yellow precipitate; the filtrate has an acid reaction.

| | *At* 100°. | | Löwig & Weidmann. |
|---|---|---|---|
| 9 PbO | 1006·2 | 85·69 | 84·73 |
| $C^{14}NH^4O^7$ | 168·0 | 14·31 | |
| $C^{14}NH^4O^7,9PbO$ | 1174·2 | 100·00 | |

The solution of the soda-salt forms a light green precipitate with copper-salts and colours ferric salts cherry-red. (Pagenstecher, Löwig.)

The acid dissolves readily in *alcohol* and *ether*.

## Nitrosalicylic Acid.

$C^{14}NH^5O^{10} = C^{14}XH^5O^2,O^4$.

FOURCROY & VAUQUELIN. (1806.) *Ann. Chim.* 55, 303 — *N. Gehl.* 2, 236.
CHEVREUL. *Ann. Chim.* 72, 131.
BUFF. *Schw.* 51, 38; 54, 163.
DUMAS. *Ann. Chim. Phys.* 63, 270; *Ann. Pharm.* 9, 79; *Pogg.* 29, 96. — *N. Ann. Chim.* 2, 224; *Ann. Pharm.* 39, 350; *J. pr. Chem.* 24, 211.
MARCHAND. *J. pr. Chem.* 26, 385; *Pharm. Centr.* 1842, 883.
PROCTER. *N. J. Pharm.* 3, 285; *Pharm. Centr.* 1843, 700.

CAHOURS. *N. Ann. Chim. Phys.* 7, 225; *Ann. Pharm.* 48, 61, *J. pr. Chem.* 29, 198.
PIRIA. *Ann. Pharm.* 56, 35.
GERHARDT. *N. Ann. Chim. Phys.* 7, 225; *J. pr Chem.* 28, 84.
STENHOUSE. *Phil. Mag. J.* 33, 231; *Ann. Pharm.* 70, 253; *J. pr. Chem.* 45, 192; *Pharm. Centr.* 1848, 829.
H. MAJOR. *Das chem. Laboratorium der Univ. Christiania.* 1854, s. 84.

***Chevreul's Volatile acid from Indigo, or Artificial Bitter with minimum of acid, Indigotic acid, Artificial Indigotic acid, Anilic acid, Nitroanilic acid, Anilsalpetersäure, Nitrospiroylic acid, Anilotic acid.***

**Discovered by Fourcroy & Vauquelin and regarded as benzoic acid. First more accurately investigated by Buff (1827).**

*Formation.* 1. By the action of hot and moderately dilute nitric acid on indigo-blue. (Fourcroy & Vauquelin, Chevreul.) — 2. By the action of fuming nitric acid on salicylic acid. (Gerhardt.) — 3. By the action of cold dilute nitric acid on salicin, with simultaneous formation of helicin. (Piria, Major.)

*Preparation.* 1. Powdered indigo is gradually added to a boiling mixture of 1 pt. fuming nitric acid and 10 to 15 pts. of water, as long as any evolution of gas is thereby produced (with a stronger acid, as Chevreul used it, large quantities of picric acid and artificial tannic acid are produced); the liquid is then boiled for a while, the water being renewed as it evaporates, and filtered hot; the brown-red residue containing undecomposed indigo, a brown-red substance (smaller in quantity as the indigo is purer) and nitrosalicylic acid, is repeatedly boiled with pure water and ultimately with water containing nitric acid to extract the nitrosalicylic acid; and the united yellow filtrates are left to cool. The flakes of impure nitrosalicylic acid which separate on cooling are pressed and dissolved in hot water; the oily drops which rise to the surface are removed by means of bibulous paper; the warm solution is decanted from the impurities which have sunk to the bottom (from which, however, a considerable quantity of nitrosalicylic acid may still be extracted by hot water), and then left to cool; the nitrosalicylic acid which has crystallised in needles is dissolved in a large quantity of hot water; and carbonate of lead is gradually added to the solution till carbonic acid is no longer evolved from it, and the liquid remains turbid after the brown film which forms on each addition has been removed (if an excess of carbonate of lead is added, a basic lead-salt is precipitated together with a lead-compound of the resin with which the acid is contaminated.) The warm filtrate becomes turbid, and after a few minutes deposits red drops of liquid, and the solution decanted therefrom deposits, after 12 hours, a rather large quantity of nitrosalicylate of lead, which may be recrystallised; the mother-liquor still yields a considerable quantity of salt. On decomposing the warm aqueous solution of the lead-salt with sulphuric acid, nitrosalicylic acid csystallises from the liquid in needles having a faint yellowish tint. Perfectly colourless needles are obtained by decomposing the turbid solution of the lead-salt with nitric acid. (Chevreul, Buff, Marchand.)

2. Fuming nitric acid is poured, with constant stirring, upon salicylic acid contained in a vessel surrounded by cold water, till fresh additions of acid produce no further action, and the reddish yellow resinous mass

thus produced is washed with cold water, dissolved in boiling water, and left to crystallise by cooling. (Gerhardt, Marchand.)

3. Methylnitrosalicylic acid is decomposed by boiling with potash, the brown-red liquid supersaturated with weak hydrochloric acid, and the separated flakes of the acid crystallised. (Cahours.)

4. When one pt. of pulverised salicin is shaken up with 10 pts. of nitric acid of 50° Bm. till the whole is dissolved, and the solution is left to stand in a stoppered bottle at a temperature of 10° to 15°, it deposits crystals after a while, the quantity continuing to increase for more than a week; they dissolve for the most part in ether, leaving a residue of helicin. The ethereal solution yields, by evaporation, crystals of nitrosalicylic acid having a faint yellowish colour. (H. Major). Piria, by treating salicin in the same manner in open vessels obtained, together with helicin, only traces of nitrosalicylic (anilotic) acid.

*Properties.* Colourless needles having a bitter, rough, somewhat acid taste, a slightly sour, pungent odour and feeble acid reaction. (Chevreul, Buff.) Melts when gently heated and crystallises in six-sided tables on cooling. Sublimes even at a gentle heat, and if the heat be carefully applied, may be completely volatilised without decomposition.

| | | | Buff. | Dumas. | Gerhardt. | Cahours. |
|---|---|---|---|---|---|---|
| 14 C | 84 | 45·90 | 46·27 | 45·73 | 45·32 | 45·55 |
| N | 14 | 7·65 | 7·48 | 7·78 | | 7·55 |
| 5 H | 5 | 2·73 | 2·11 | 2·76 | 2·83 | 2·98 |
| 10 O | 80 | 43·72 | 44·14 | 43·73 | | 43·92 |
| $C^{14}NH^5O^{10}$ | 183 | 100·00 | 100·00 | 100·00 | | 100·00 |

Marchand.

| | a. | b. | c. | d. |
|---|---|---|---|---|
| C | 45·49 | 45·27 | 45·88 | 45·88 |
| N | | 7·67 | 7·69 | 7·70 |
| H | 2·75 | 2·94 | 2·76 | 2·81 |
| O | | 44·12 | 43·67 | 43·61 |
| | | 100·00 | 100·00 | 100·00 |

The acid analysed by Buff and by Dumas was prepared from indigo. Marchand dried his acid *a* at the temperature of the air; *b* at 150° and *c* at 230°; *d* was prepared from salicylic acid; so likewise was that which Gerhardt analysed. Cahours prepared his acid from oil of wintergreen.

*Decompositions.* 1. The acid suffers partial decomposition when quickly heated, giving off carbonic acid and nitrogen, and leaving a large quantity of charcoal, which quickly burns away in contact with the air. (Chevreul.) — 2. Heated in the air, it takes fire very readily and burns with a very sooty flame. (Buff.) — 3. The dry acid is not decomposed by *chlorine gas.* (Buff.) — Chlorine gas passed into the hot aqueous solution converts it in a few days into chloranil. (Stenhouse.) — 4. Boiled with *chlorate* of potash and *hydrochloric* acid, it immediately yields chloranil and carbonic acid. (Stenhouse, Hofmann.) Boiled with *chloride of lime,* it yields in a few minutes chloropicrin (but not under 100°). (Stenhouse, *Ann. Pharm.* 78, 5.) — 5. Strong *nitric acid* decomposes nitrosalicylic acid by boiling, into oxalic and picric acids. (Buff.) — 6. Hot *oil of vitriol* forms a brown solution from which water throws down brown flakes. — 7. In contact with *nascent hydrogen,* the acid dissolves in water, forming a blood-red solution, which after a while

deposits purple-red flakes. (Buff.) — 8. When boiled with hydrosulphate of ammonia, it is rapidly decomposed in a similar manner to nitronaphthalin. (Piria.)

*Combinations.* *a.* With *Water.*

*Hydrated Nitrosalicylic acid.* — Colourless needles (Chevreul, Buff); if the hydrate has a yellowish tint while moist, it is contaminated with picric acid. (Dumas.) By exposure for some time to dry air, it loses 2 At. water; in vacuo at 100°, it gives off 10·72 p. c. and at 150°, 11·6 p. c., a portion of the acid evaporating at the same time. (Marchand.) (Calculation gives for 2 At. water of crystallisation, a loss of 8·95 p. c.)

| *Crystallised.* | | | Marchand. *a.* | Marchand. *b.* |
|---|---|---|---|---|
| 14 C | 84 | 41·79 | 42·74 | 41·43 |
| N | 14 | 6·96 | | |
| 7 H | 7 | 3·48 | 3·57 | 3·57 |
| 12 O | 96 | 47·77 | | |
| $C^{14}NH^5O^{10} + 2Aq$ | 201 | 100·00 | | |

*a* was prepared from indigo, *b* from salicylic acid.

*Aqueous Nitrosalicylic acid.* — The acid dissolves in 1000 pts. of cold water, and in all proportions of hot water. The solution is colourless. (Buff.)

*b.* With *Bases.* — The neutral nitrosalicylates are $C^{14}XH^3M^2O^6$; they are mostly yellow, take fire when heated, without actual detonation, and burn like gunpowder. They redden ferric salts strongly.

*Nitrosalicylate of Ammonia.* — The acid is saturated with ammonia and the hot saturated solution abandoned to spontaneous evaporation. Beautiful golden-yellow or orange-yellow needles. Anhydrous, gives off ammonia when heated, but afterwards the free acid sublimes.

| | | | Dumas. | Marchand. |
|---|---|---|---|---|
| 14 C | 84 | 42 | 42·1 | 41·80 |
| 2 N | 28 | 14 | 13·7 | 14·34 |
| 8 H | 8 | 4 | 4·1 | 4·06 |
| 10 O | 80 | 40 | 40·1 | 39·80 |
| $C^{14}XH^4(NH^4)O^6$ | 200 | 100 | 100·0 | 100·00 |

*Nitrosalicylate of Potash.* — When the acid is dissolved in aqueous potash (if not quite pure it colours the liquid brown), and the solution evaporated, it solidifies in a silky crystalline web, which, when washed with cold water and pressed, yields light yellow crystals. The salt dissolves readily in boiling water, sparingly in cold water and in alcohol. (Marchand.) Chevreul obtained the salt in red crystals; Buff, in orange-yellow needles.

| | | | Marchand. |
|---|---|---|---|
| KO | 47·2 | 21·34 | 21·32 |
| $C^{14}NH^4O^9$ | 174·0 | 78·66 | |
| $C^{14}XH^4KO^6$ | 221·2 | 100·00 | |

*Nitrosalicylate of Soda.* — Yellow crystals soluble in water.

*Nitrosalicylate of Baryta.* — *a. Neutral.* — 1. Obtained by continuous heating of the salt *b*. (Marchand.) 2. By boiling *b* with baryta-water. (Marchand.) — 3. By boiling the hot aqueous solution of *b* with ammonia. (Buff.) — Yellow powder resembling chromate of lead. Dissolves sparingly in cold, somewhat more readily in hot water. (Buff.)

| | | | Buff. | Marchand. |
|---|---|---|---|---|
| 2 BaO | 153·2 | 41·15 | 41·04 | 41·26 |
| $C^{14}NH^{3}O^{6}$ | 165·0 | 44·32 | | |
| 6 HO | 54·0 | 14·53 | | |
| $C^{14}XH^{3}Ba^{2}O^{6}$ + 6Aq | 372·2 | 100·00 | | |

*b. Acid.* — The aqueous acid is boiled with carbonate of baryta, and the hot-filtered solution left to cool. If the acid is not quite pure, a yellow powder remains mixed with the insoluble carbonate of baryta. (Marchand.) — Beautiful shining needles united in tufts. (Buff, Marchand.) Contains 5 At. water, four of which are given off at 200°, the remainder only when the salt begins to decompose. At a strong red heat, the salt decomposes, with strong intumescence but without detonation, throwing out carbonaceous pyrophoric masses, which immediately burn away when exposed to the air and leave carbonate of baryta. (Marchand.)

| *At 200°.* | | | Marchand. *from indigo.* | Marchand. *from salicylic acid.* |
|---|---|---|---|---|
| BaO | 76·6 | 29·51 | 30·34 | 30·56 |
| $C^{14}NH^{4}O^{6}$ | 174·0 | 67·02 | | |
| HO | 9·0 | 3·47 | | |
| $C^{14}NH^{4}BaO^{10}$ + Aq | 259·6 | 100·00 | | |

| *Crystallised.* | | | Marchand. |
|---|---|---|---|
| BaO | 76·6 | 25·92 | 25·57 |
| $C^{14}NH^{4}O^{9}$ | 174·0 | 58·87 | |
| HO | 9·0 | 3·04 | |
| 4 HO | 36·0 | 12·17 | 12·67 |
| $C^{14}NH^{4}BaO^{10}$ + 5Aq | 295·6 | 100·00 | |

The nitrosalicylates of *strontia, lime,* and *magnesia,* are yellow and dissolve readily in water. (Buff.)

*Nitrosalicylate of Lead.* — *a. Neutral.* — Obtained by treating the salt *c* with hot ammonia. Dark yellow, very fine powder, perfectly insoluble. (Buff, Dumas.)

| | | | Buff. | Dumas. |
|---|---|---|---|---|
| 2 PbO | 223·6 | 56·24 | 56·14 | 55·3 |
| $C^{14}NH^{4}O^{9}$ | 174·0 | 43·76 | | |
| $C^{14}NH^{3}Pb^{2}O^{10}$ + Aq | 397·6 | 100·00 | | |

*b. Sesquibasic.* — When nitrate of lead is added to a hot solution of excess of nitrosalicylate of potash, the liquid deposits delicate needles of

a deep yellow colour, insoluble in water, whether hot or cold, but soluble in free nitrosalicylic acid. The salt is obtained in a less pure state by digesting the aqueous solution of the acid with carbonate of lead. (Buff.)

| | | | | Buff. | Dumas. |
|---|---|---|---|---|---|
| 3 PbO | 335·4 | .... | 49·08 | 51·03 | 50 |
| 2 $C^{14}NH^4O^9$ | 348·0 | .... | 50·92 | | |
| $3PbO,2C^{14}NH^4O^9$ | 683·4 | .... | 100·00 | | |

*c. Acid.* — 1. Obtained by gradually adding nitrosalicylate of potash to an excess of hot aqueous nitrate of lead. — 2. When carbonate of lead is added to a hot aqueous solution of nitrosalicylic acid till the effervescence becomes slow and a few yellow flakes separate, the liquid, if filtered hot, deposits the acid salt in crystals as it cools. — By the first process: pale yellow bulky precipitate, which, after washing with cold water and drying, presents the appearance of a pale yellow crystalline mass. — The second process yields yellow ill defined crystals. — The salt is somewhat more soluble in water than the free acid, so that on adding nitric acid to its solution, nitrosalicylic acid is precipitated. (Buff.)

| | | | | Buff. (1) | Buff. (2) |
|---|---|---|---|---|---|
| PbO | 111·8 | .... | 37·92 | 37·38 | 36·43 |
| $C^{14}NH^4O^9$ | 174·0 | .... | 59·02 | | |
| HO | 9·0 | .... | 3·06 | | |
| $C^{14}XH^4PbO^6$ + Aq | 294 8 | .... | 100·00 | | |

*Ferric Nitrosalicylate.* — The aqueous acid forms a hyacinth-red solution with erric oxide and reddens ferric salts. (Chevreul.) Ferric nitrosalicylate crystallises in dark red, almost black red needles, which dissolve sparingly in cold water, forming a blood-red solution. (Buff.)

*Cupric Nitrosalicylate.* — The aqueous acid dissolves cupric oxide very readily; but the salt is soluble only in hot water, and separates again in green flakes on cooling. (Buff.)

*Mercurous Nitrosalicylate.* — The potash-salt forms with mercurous nitrate a pale yellow precipitate, which is not easily decomposed by hydrochloric acid. It is insoluble in cold, and sparingly soluble in hot water. (Buff.)

| | | | | Buff. |
|---|---|---|---|---|
| $Hg^2O$ | 208 | .... | 44·06 | 43·26 |
| $C^{14}NH^4O^9$ + 10HO | 264 | .... | 55·94 | |
| $C^{14}XH^4Hg^2O^6$ + 10Aq | 472 | .... | 100·00 | |

*Nitrosalicylate of Silver.* — The aqueous acid dissolves oxide of silver at the boiling heat, but the solution blackens if the boiling be too long continued. (Chevreul.) Neither nitrosalicylic acid nor nitrosalicylate of potash precipitates nitrate of silver. Nitrosalicylate of ammonia produces with nitrate of silver a light yellow precipitate which dissolves

pretty readily in boiling water; the solution effloresces slightly when evaporated. (Dumas, Marchand.) Small light red needles, soluble with difficulty in cold water. (Buff.) Straw-coloured needles united in stellate groups. (Marchand); they become darker in colour by exposure to light. (Major.)

| | | | | Dumas. | Marchand. | Major. |
|---|---|---|---|---|---|---|
| Ag | 108·1 | 37·26 | | 36·66 | 36·80 | 37·05 |
| 14 C | 84·0 | 28·95 | | 29·22 | 29·00 | 29·20 |
| N | 14·0 | 4·83 | | | 4·45 | |
| 4 H | 4·0 | 1·38 | | 1·56 | 1·54 | 1·50 |
| 10 O | 80·0 | 27·58 | | | 28·21 | |
| $C^{14}XH^4AgO^6$ | 290·1 | 100·00 | | | 100·00 | |

The salt does not detonate when heated, but throws out shoots of carburet of silver, which burns and leaves pure silver. (Marchand.)

The acid dissolves in *alcohol*, in all proportions at the boiling heat.

## Methylnitrosalicylic Acid.

$C^{16}NH^7O^{10} = C^2H^3O,C^{14}XH^4O^8$.

CAHOURS. (1844.) *N. Ann. Chim. Phys.* 10, 345; *Pharm. Centr.* 1844, 438.

*Nitrosalicylformester, Anilate or Indigotate of Methylène.*

When fuming nitric acid is added to methylsalicylic acid, cooled so that no spirting may take place, the liquid soon solidifies in a crystalline mass from which the free nitric acid may be extracted by boiling water: the product may be purified by two or three crystallisations from alcohol. (Cahours.)

Very delicate yellowish needles which melt between 88° and 90°, and may for the most part be volatilised without decomposition.

| | | | Cahours. |
|---|---|---|---|
| 16 C | 96 | 48·73 | 48·53 |
| N | 14 | 7·10 | 7·27 |
| 7 H | 7 | 3·55 | 3·55 |
| 10 O | 80 | 40·62 | 40·65 |
| $C^{16}NH^7O^{10}$ | 197 | 100·00 | 100·00 |

*Decompositions.* 1. When fuming nitric acid in slight excess is gradually added to methylnitrosalicylic acid, a brisk action takes place, and a dark red solution is formed. If the mixture be not cooled but gently heated at the last, the liquid becomes turbid and deposits drops of oil, which, if the heat be discontinued as soon as they cease to increase, form a yellow resinous mass; and this substance when dissolved in hot alcohol, separates almost completely on cooling in pale yellow needles which melt at 95°, and form on cooling a yellow radiated mass, which, if carefully raised to a higher temperature, sublimes in pale yellow slender needles; it dissolves sparingly and with slight

colour in cold water, and more abundantly in hot water, whence it separates in long, slender, nearly colourless crystals; it dissolves also in alcohol and ether, especially when hot. Neither the aqueous solution nor the acid obtained after decomposition with potash reddens ferric salts. The crystals contain 43·40 p. c. C, 9·57 N, and 3·28 H, and are therefore a mixture of methylnitrosalicylic and methylbinitrosalicylic acids. (Cahours.) Procter obtained a similar substance by boiling wintergreen oil with nitric acid of sp. gr. 1·4.

2. Boiled with *potash-ley*, it yields methylic alcohol and nitrosalicylate of potash. (Cahours.)

3. It does not dissolve immediately in *ammonia*, but after three weeks a yellowish red solution is formed containing nitrosalicylamide. (Cahours.)

*Combinations.* 1. The acid dissolves but very sparingly in *water;* it melts in boiling water, and the liquid on cooling deposits very slender pale yellow needles. — 2. It dissolves readily in *potash* or *soda*, forming a methylnitrosalicylate. (Cahours.)

It dissolves pretty readily in boiling *alcohol*, the solution solidifying as it cools. (Cahours.)

## Ethylnitrosalicylic Acid.

$C^{18}NH^9O^{10} = C^4H^5O,C^{14}NH^{14}O^9$.

CAHOURS. (1844.) *N. Ann. Chim. Phys.* 10, 367.

*Nitrosalicylvinester, Indigotic ether.*

When fuming nitric acid is gradually added to salicylate of ethyl, which is kept cool, a red liquid is formed from which water throws down a heavy oil solidifying after a while in a crystalline mass. The oil sometimes remains liquid for several days, but immediately solidifies, when a few drops of ammonia are added to saturate the free acid. When the solid mass is repeatedly washed with cold water and dissolved in hot alcohol, the solution yields by evaporation yellow silky crystals which must be repeatedly recrystallised.

Yellowish needles, very much resembling methylnitrosalicylic acid. Melts in boiling water, and solidifies again on cooling.

| | | | Cahours. |
|---|---|---|---|
| 18 C | 108 | 51·19 | 50·94 |
| N | 14 | 6·64 | 6·64 |
| 9 H | 9 | 4·26 | 4·31 |
| 10 O | 80 | 37·91 | 38·11 |
| $C^{18}NH^9O^{10}$ | 211 | 100·00 | 100·00 |

*Decompositions.* 1. Heated with *potash* or *soda*, it yields nitrosalicylic acid and alcohol. — 2. It is not immediately dissolved by *ammonia*, but when left in contact with it in a closed vessel, it gradually dissolves, forming nitrosalicylamide and alcohol.

*Combinations.* The acid dissolves in cold *potash* or *soda*, forming an ethylnitrosalicylate of the alkali.

*Appendix to Nitrosalicylic Acid.*

## Nitroxybenzoic Acid.

$C^{14}NH^5O^{10} = C^{14}XH^5O^2,O^4$.

GERLAND. *Ann. Pharm.* 91, 192; *Pharm. Centr.* 1854, 829.

Oxybenzoic acid is treated with nitric acid of sp. gr. 1·36, and the excess of nitric acid evaporated over the water-bath. The solution of the yellow residue in hot water yields beautiful yellow rhombic crystals having an unpleasant bitter taste; they may be purified by repeated crystallisation from hot water.

| | | | | Gerland. |
|---|---|---|---|---|
| 14 C | 84 | 45·90 | | 45·95 |
| N | 14 | 7·65 | | |
| 5 H | 5 | 2·73 | | 3·17 |
| 10 O | 80 | 43·72 | | |
| $C^{14}NH^5O^{10}$ | 183 | 100·00 | | |

When acted upon by strong nitric acid, it yields substitution-products in which 2 or 3 At. H are replaced by $NO^4$, and which detonate with great violence when heated.

The acid dissolves readily in hot water. The solution has a strong yellow colour even when dilute.

The acid expels carbonic acid from its compounds and forms crystallisable salts.

*Nitroxybenzoate of Potash.* — Crystallises readily in beautiful yellow shining prisms or needles, very much like picrate of potash. It dissolves very sparingly in cold, readily in boiling water. Gives off its water of crystallisation at 100°.

| | | | | Gerland. |
|---|---|---|---|---|
| KO | 47·2 | 21·34 | | 21·62 |
| $C^{14}NH^4O^5$ | 174·0 | 78·66 | | |
| $C^{14}NH^4KO^6$ | 121·2 | 100·00 | | |

Decomposes with slight detonation when heated.

*Oxynitro-nucleus* $C^{14}X^2H^4O^2$.

## Binitrosalicylic Acid.

$C^{14}N^2H^4O^{14} = C^{14}X^2H^4O^2,O^4$.

CAHOURS. (1849.) *N. Ann. Chim. Phys.* 25, 11; *Ann. Pharm.* 69, 232; *J. pr. Chem.* 46, 325; abstr. *Compt. rend.* 27, 485; *Pharm. Centr.* 1849, 163.

STENHOUSE. *Phil. Trans.* 1851, 143; *Ann. Pharm.* 78, 1; *Pharm. Centr.* 1851, 434.

*Nitropopulinsäure, Acide nitrosalicylique binitré.*

*Formation.* 1. By the action of nitrosulphuric acid on methylsalicylic acid. (Cahours.) — 2. By heating the aqueous extract of the branches of *Populus balsamifera* or *Populus nigra* with dilute nitric acid. (Stenhouse.)

*Preparation.* 1. *From Methylbinitrosalicylic acid.* — When methylbinitrosalicylic acid is boiled for a few minutes with strong caustic potash, a brown-red solution is formed, which on cooling deposits red binitrosalicylate of potash. This salt, or the yellow salt obtained from it by boiling with dilute nitric acid, is treated with fuming oil of vitriol at a temperature below 50°, whereby sulphate of potash is produced. The binitrosalicylic acid is precipitated from the solution by cold water. (Cahours.)

2. *From Nitropopulic acid.* — The chopped branches of *Populus balsamifera* or *Populus nigra* are exhausted with boiling water, the dark brown bitter liquid evaporated to an extract, and this extract heated for 24 hours with dilute nitric acid, whereupon large quantities of nitrous vapours are evolved with a pleasant aromatic odour. At the boiling heat nothing but picric acid would be formed. The liquid is evaporated to dryness over the water-bath, the residue dissolved in a large quantity of hot water, and the liquid filtered through a cloth after cooling—whereupon it deposits a large quantity of resin, which when treated with nitric acid, still yields a large quantity of binitrosalicylic acid. — The clear liquid is then concentrated over the water-bath, and after cooling, exactly neutralised with carbonate of potash, whereupon it gradually deposits picrate and binitrosalicylate of potash in crystals, while oxalate and nitrate of potash remain dissolved. The crystals are washed with cold water, pressed and triturated with a small quantity of cold dilute carbonate of potash, which dissolves the binitrosalicylate of potash; the solution is filtered from the picrate of potash and slightly supersaturated with hydrochloric acid; the binitrosalicylate of potash, which is precipitated in the form of a crystalline powder, is washed with a small quantity of water, and redissolved in a very small quantity of carbonate of potash, which again leaves picrate of potash undissolved; the binitrosalicylate of potash precipitated with hydrochloric acid, and repeatedly crystallised from hot water with addition of animal charcoal; and the now light yellow salt is boiled with a large quantity of hydrochloric acid. Binitrosalicylic acid then crystallises out, still contaminated with a yellow substance which adheres to it closely, but may be removed by crystallisation, first from hot hydrochloric acid, then from hot water, with addition of animal charcoal. The crystals are quickly freed from the mother-liquor, pressed between paper, and dried in vacuo.

*Properties.* By slow crystallisation it forms small, hard, colourless prisms; by quick cooling, needles having a silky lustre. Melts at a gentle heat and sublimes undecomposed when carefully heated. (Cahours, Stenhouse.) The air-dried crystals give off in vacuo 7·21 per cent. of water (2 At. calc. 7·31 p. c.) (Stenhouse.)

| | | | Cahours. | Stenhouse. *from Pop. bals.* | Stenhouse. *from Pop. nigra.* |
|---|---|---|---|---|---|
| 14 C | 84 | 36·84 | 36·81 | 36·71 | 36·81 |
| 2 N | 28 | 12·30 | 12·25 | 12·23 | |
| 4 H | 4 | 1·75 | 1·85 | 1·75 | 1·90 |
| 14 O | 112 | 49·11 | 49·09 | 49·31 | |
| $C^{14}N^{2}H^{4}O^{12}$ | 228 | 100·00 | 100·00 | 100·00 | |

*Decompositions.* 1. In contact with the air, it burns with a bright flame. (Stenhouse.) — 2. Exposed to the air in the moist state, it quickly turns yellow. (Stenhouse.) — 3. By boiling with strong *nitric acid*, it is quickly converted into picric acid. (Cahours, Stenhouse.) — 4. Boiled with hydrochloric acid and chlorate of potash, it forms chloranil. (Stenhouse.) — 5. It is not decomposed by chloride of lime at ordinary temperatures, but if the liquid be boiled, violent effervescence takes place and chloropicrin is given off in abundance. (Stenhouse.) — 6. The solution in oil of vitriol decomposes at 100°, giving off sulphurous acid and leaving a carbonaceous mass. (Cahours.)

*Combinations.* The acid is nearly insoluble in cold water but dissolves abundantly in hot water. (Cahours.) It dissolves readily in water, forming a yellow solution. (Stenhouse.)

It dissolves without decomposition in slightly heated oil of vitriol, and is precipitated by water. (Cahours.) In dilute sulphuric and hydrochloric acid, it is less soluble than in water, forming pale yellow solutions which become deeper in colour when further diluted. (Stenhouse.)

The binitrosalicylates are mostly yellow and sparingly soluble in water. They detonate violently when heated. The formula of the neutral salts is $C^{14}X^2H^2M^2O^6$.

*Binitrosalicylate of Ammonia.* — The acid dissolves readily in ammonia, and the solution when evaporated forms beautiful small yellow needles. (Cahours.) It is somewhat more soluble in water than the potash-salt. (Stenhouse.)

| | | | Cahours. |
|---|---|---|---|
| 14 C | 84 | 34·28 | 34·46 |
| 3 N | 42 | 17·14 | 17·38 |
| 7 H | 7 | 2·85 | 2·78 |
| 14 O | 112 | 45·73 | 45·38 |
| $C^{14}X^2H^2(NH^4)O^6$ | 245 | 100·00 | 100·00 |

*Binitrosalicylate of Potash.* — *a. Neutral.* — Produced when methylnitrosalicylic acid is decomposed by boiling with excess of strong potash-ley. Beautiful needles having a splendid yellowish red colour and satiny lustre, and united in stellate groups. Appears to be completely decomposed by continued boiling with potash. Detonates violently on glowing coals or on a hot plate. (Cahours.)

| | | | Cahours. |
|---|---|---|---|
| 2 KO | 94·4 | 30·05 | |
| 14 C | 84·0 | 26·83 | 26·15 |
| 2 N | 28·0 | 8·95 | 9·05 |
| 3 H | 3·0 | 0·95 | 1·06 |
| 13 O | 104·0 | 33·22 | |
| $C^{14}X^2H^2K^2O^6 + Aq$ | 313·4 | 100·00 | |

*b. Monobasic.* — Produced by neutralising the aqueous acid with carbonate of potash. (Stenhouse), or by heating *a* with dilute nitric acid; it then separates on cooling. (Cahours.) Small lemon-yellow prisms. (Stenhouse.) — The salt dissolves very sparingly in cold water,

and not at all in alcohol or ether. (Cahours.) It dissolves very readily in alkaline liquids and is precipitated therefrom by acids.( Stenhouse.) It deposits the free acid when boiled with strong hydrochloric acid. (Stenhouse.) It dissolves in slightly heated oil of vitriol, and the solution, on being mixed with water, deposits the acid in crystalline laminæ. (Cahours.) It detonates on glowing coals, but not so strongly as *a*.

| | | | Cahours. | Stenhouse. |
|---|---|---|---|---|
| KO | 47·2 | 17·66 | 17·46 | 17·49 |
| 14 C | 84·0 | 31·58 | 31·32 | 31·47 |
| 2 N | 28·0 | 10·53 | 10·33 | |
| 3 H | 3·0 | 1·13 | 1·17 | 1·17 |
| 13 O | 104·0 | 39·10 | 39·72 | |
| $C^{14}X^2H^3KO^6$ | 266·2 | 100·00 | 100·00 | |

*Binitrosalicylate of Soda.* — Obtained by neutralising the aqueous acid with carbonate of soda. (Stenhouse.) Small spicular crystals. (Stenhouse.) Yellow shining needles (Cahours.) More soluble in water than the potash-salt.

| | | | Stenhouse. |
|---|---|---|---|
| NaO | 31 | 12·40 | 12·34 |
| $C^{14}N^2H^3O^{13}$ | 219 | 87·60 | |
| $C^{14}X^2H^3NaO^6$ | 250 | 100·00 | |

*Binitrosalicylate of Baryta.* — *a. Neutral.* — Boiling baryta-water is added to the boiling aqueous solution of the acid as long as a precipitate is formed; this precipitate is then quickly washed with hot water and dried in vacuo. Very small crystals.

| | | | Stenhouse. |
|---|---|---|---|
| 2 BaO | 153·2 | 41·16 | 41·12 |
| $C^{14}N^2H^3O^{13}$ | 219·0 | 58·84 | |
| $C^{14}X^2H^2Ba^2O^6$ + Aq | 372·2 | 100·00 | |

*b. Acid.* — Baryta-water is added to the hot aqueous acid as long as the resulting precipitato redissolves on agitation. The solution on cooling yields crystalline grains which are dried, first in vacuo, afterwards over the water-bath.

| | | | Stenhouse. |
|---|---|---|---|
| BaO | 76·6 | 25·91 | 25·84 |
| $C^{14}N^2H^3BaO^{12}$ | 219·0 | 74·09 | |
| $C^{14}X^2H^3BaO^6$ | 295·6 | 100·00 | |

The aqueous acid colours *ferrous* salts yellow, *ferric* salts dark red.

The potash-salt precipitates neutral and basic acetate of *lead* with the aid of heat. (Stenhouse.)

*Binitrosalicylate of Silver.* — Separates in small crystalline grains from the solution of carbonate of silver in the aqueous acid. (Cahours, Stenhouse.)

| | | | | Cahours. | Stenhouse. |
|---|---|---|---|---|---|
| Ag | 108 | 32·24 | | 32·00 | 34·28 |
| 14 C | 84 | 25·07 | | 24·89 | 24·84 |
| 2 N | 28 | 8·36 | | | |
| 3 H | 3 | 0·89 | | 1·14 | 0·94 |
| 14 O | 112 | 33·44 | | | |
| $C^{14}X^2H^3AgO^6$ | 335 | 100·00 | | | |

The acid dissolves in alcohol whether weak or strong, more readily than in water. (Stenhouse.) It is very sparingly soluble in alcohol and ether. (Cahours.)

## Methylbinitrosalicylic Acid.

$C^{16}N^2H^6O^{14} = C^2H^3O,C^{14}X^2H^3O^6$.

CAHOURS. (1849.) *Compt. rend.* 27, 485.—*N. Ann. Chim. Phys.* 25, 6; *Ann. Pharm.* 69, 230; *J. pr. Chem.* 46, 321; *Pharm. Centr.* 1849, 161.

***Binitrosalicylformester, Acide gaulthérique binitrique, Salicylate de methylène binitrique.***

*Formation and Preparation.* When methylsalicylic acid is dropped into a mixture of fuming nitric acid and fuming oil of vitriol kept cool by cold water, a clear dark orange-coloured liquid is produced. As soon as the drops of methylsalicylic acid cease to dissolve, a small quantity more of nitrosulphuric acid is added, the mixture shaken till the solution is complete, and the liquid after some minutes diluted with eight times the quantity of water, whereupon the methylbinitrosalicylic acid separates out and may be crystallised from solution in boiling alcohol. The aqueous mother-liquor contains methylternitrosalicylic acid.

*Properties.* Yellowish white crystalline scales which become nearly colourless after two crystallisations. Heavier than water. Melts between 124° and 125°, forming a pale yellowish liquid which solidifies in a fibrous mass on cooling. Volatilises completely when carefully heated in a retort, and sublimes in very delicate shining laminæ.

| | | | | Cahours. |
|---|---|---|---|---|
| 16 C | 96 | 39·66 | | 39·42 |
| 2 N | 28 | 11·57 | | 11·61 |
| 6 H | 6 | 2·48 | | 2·54 |
| 14 O | 112 | 46·29 | | 46·43 |
| $C^{16}X^2H^6O^6$ | 242 | 100·00 | | 100·00 |

*Decompositions.* 1. When suddenly heated, it detonates, and decomposes completely, emitting a black smoke and leaving a copious carbonaceous residue.—2. By continued boiling, either with fuming or with commercial nitric acid, it is completely decomposed, with formation of picric acid. By the continued action of nitrosulphuric acid, it is converted into methylternitrosalicylic acid.—3. Its solution in oil of vitriol

gives off carbonic acid between 75° and 80°; if it be gradually heated and too great a rise of temperature prevented by frequent immersion in cold water, a colourless liquid is formed, which is rendered turbid by addition of a large quantity of water, and on cooling yields small shining needles, which dissolve readily in boiling water or alcohol, and crystallise on cooling. — If the solution in oil of vitriol be heated somewhat more quickly or above 100°, the liquid turns red and ultimately black, giving off carbonic and sulphurous acids, and deposits brown flakes when mixed with water. — 4. Boiled with strong potash-ley, it forms binitrosalicylate of potash and methylic alcohol.

*Combinations.* The acid is insoluble in water, even at the boiling heat.

It dissolves in gently heated oil of vitriol, and is precipitated therefrom by water in nearly colourless scales having a strong lustre.

It does not dissolve in nitric acid either dilute or concentrated. — It dissolves without decomposition in fuming nitric acid at temperatures between 30° and 40°, and is reprecipitated by water in its original state. The solution in gently heated nitrohydrochloric acid deposits on cooling needles of the unaltered substance.

With salifiable bases, the acid forms the *methylbinitrosalicylates* (*Gaulthérates binitriques.*)

*Methylbinitrosalicylate of Ammonia.* — The acid dissolves in heated ammonia, and the solution on cooling deposits yellow transparent needles, which dissolve sparingly in cold, readily in hot water. Acids precipitate the methylbinitrosalicylic acid in its original state.

| | | | | Cahours. |
|---|---|---|---|---|
| 16 C | 96 | | 37·07 | 36·97 |
| 3 N | 42 | | 16·21 | |
| 9 H | 9 | | 3·47 | 3·47 |
| 14 O | 112 | | 43·25 | |
| $C^{16}X^{2}H^{5}(NH^{4})O^{6}$ | 259 | | 100·00 | |

Methylbinitrosalicylic acid dissolves without decomposition in dilute *potash* or *soda*-ley, forming salts which crystallise by evaporation.

*Methylbinitrosalicylate of Silver.* — Nitrate of silver added to a dilute aqueous solution of the ammonia-salt, forms a beautiful yellow pulverulent precipitate, which may be washed with water and dried in vacuo.

| | | | | Cahours. |
|---|---|---|---|---|
| 16 C | 96 | | 27·50 | 27·15 |
| 2 N | 28 | | 8·02 | |
| 5 H | 5 | | 1·43 | 1·37 |
| Ag | 108 | | 30·94 | 31·24 |
| 14 O | 112 | | 32·11 | |
| $C^{16}X^{2}H^{5}AgO^{6}$ | 349 | | 100·00 | |

Methylbinitrosalicylic acid is nearly insoluble in cold alcohol, but dissolves readily in that liquid at the boiling heat.

## Ethylbinitrosalicylic Acid.

$C^{18}N^2H^8O^6 = C^4H^5O,C^{14}X^2H^3O^5$.

CAHOURS. (1849.) *N. Ann. Chim. Phys.* 25, 19; 27, 463; *Ann. Pharm.* 69, 235; 74, 313; *J. pr. Chem.* 46, 332; 49, 232; *Ann. Pharm.* 1849, 164.

*Binitrosalicylvinester, Ether salicylique binitré.*

*Formation and Preparation.*.—1. When binitrosalicylic acid is dissolved in absolute alcohol, dry hydrochloric acid gas passed into the boiling solution, the liquid evaporated to one-half, and water added, a heavy oil is thrown down which soon solidifies; and if this oil be washed several times with water and then dissolved in boiling alcohol, the solution on cooling yields crystals of ethylbinitrosalicylic acid. — 2. Ethylsalicylic acid is treated with nitrosulphuric acid in the same manner as methylsalicylic acid for the preparation of methylbinitrosalicylic acid.

*Properties.* Beautiful yellowish white scales and plates. The compound melts at a gentle heat and solidifies again in the crystalline form on cooling. After being heated for some time, it remains liquid for a considerable time on cooling and then solidifies in the form of a resin.

| | | | Cahours. (1) | Cahours. (2) |
|---|---|---|---|---|
| 18 C | 96 | 42·19 | 42·21 | 42·31 |
| 2 N | 28 | 10·94 | 10·76 | 10·70 |
| 8 H | 8 | 3·12 | 3·20 | 3·19 |
| 14 O | 112 | 43·75 | 43·83 | 43·80 |
| $C^{18}X^2H^8O^6$ | 244 | 100·00 | 100·00 | 100·00 |

Boiled with potash-ley, it yields alcohol and binitrosalicylate of potash.

With alkalis it forms soluble crystallisable salts.

*Oxynitro-nucleus* $C^{14}X^2H^3O^2$.

## Methylternitrosalicylic Acid.

$C^{16}N^3H^6O^{10} = C^2H^3O,C^{14}X^2H^3O^6$.

CAHOURS. (1849.) *Compt. rend.* 24, 553; *N. Ann. Chim. Phys.* 25, 20; *J. pr. Chem.* 46, 321; 49, 282; *Ann. Pharm.* 69, 230; 74, 313; *Pharm. Centr.* 1849, 165.

Formed by the continued action of nitrosulphuric acid on methylsalicylic acid, and is contained in the mother-liquor from which the methylbinitrosalicylic acid has crystallised out (p. 317); it separates in the crystalline form when the mother-liquor is evaporated. After solu-

tion in cold alcohol, in which the methylbinitrosalicylic acid is much less soluble, the ternitrated acid is obtained in yellow transparent tables. It is difficult to purify from picric acid.

| | | | Cahours. |
|---|---|---|---|
| 16 C | 96 | 33·45 | 32·95 |
| 3 N | 42 | 14·63 | 15·19 |
| 5 H | 5 | 1·74 | 1·61 |
| 18 O | 144 | 50·18 | 50·25 |
| $C^{16}N^3H^5O^{18}$ | 287 | 100·00 | 100·00 |

*Oxy-amidogen Nucleus* $C^{14}AdH^5O^2$.

## Salicylamic Acid.

$C^{14}NH^7O^4 = C^{14}AdH^5O^2,O^2$.

PROCTER. (1843.) *N. J. Pharm.* 3, 278; *Ann. Pharm.* 48, 69; *J. pr. Chem.* 29, 470; *Pharm. Centr.* 1843, 699.
CAHOURS. *N. Ann. Chim. Phys.* 10, 350; *Pharm. Centr.* 1854, 55, 436.
LIMPRICHT. *Ann. Pharm.* 98, 256.

*Salicylamide.*

*Formation.* By heating salicylate of ammonia; or by the action of ammonia on methylsalicylic or ethylsalicylic acid.

*Preparation.* When methylsalicylic acid is shaken up with ammonia, it gradually disappears; and the brown solution when evaporated, yields crystals which may be recrystallised from boiling alcohol. (Procter.) — The compound is not formed by the action of ammoniacal gas on oil of wintergreen. (Limpricht.) — 2. One measure of methylsalicylic acid placed for some days in a closed vessel together with 5 or 6 measures of saturated alcoholic ammonia, gradually disappears and forms a brown-yellow liquid which, when evaporated to one-half at a gentle heat, deposits long needles. On evaporating the liquid to dryness and distilling the residue, ammonia is given off at first, and afterwards a liquid collects in the upper part of the retort, which solidifies in the crystalline form on cooling; this liquid is dissolved in ether and the solution left to evaporate. (Cahours.)

*Properties.* Yellowish white laminæ having a strong lustre. Melts when gently heated and volatilises undecomposed when carefully raised to a higher temperature. Has an aromatic odour like that of aniseed and reddens litmus rather strongly. (Cahours.) Four-sided prisms with dihedral summits which melt at 118°, and at a temperature a few degrees higher, sublime without decomposition in small scales. Inodorous, or having an aromatic odour only after crystallisation from alcohol. (Procter.) — Crystallises from boiling water or alcohol in long laminæ having a yellowish colour not removable by treatment with animal charcoal. Has an acid reaction. Melts at 132°, and sublimes undecomposed at this and a somewhat higher temperature, in large colourless laminæ. (Limpricht.)

| | | | | Cahours. | Limpricht. |
|---|---|---|---|---|---|
| 14 C | 84 | | 61·31 | 61·06 | 61·5 |
| N | 14 | | 10·22 | 10·02 | 10·3 |
| 7 H | 7 | | 5·11 | 5·29 | 5·5 |
| 4 O | 32 | | 23·36 | 23·63 | 22·7 |
| $C^{14}NH^7O^4$ | 137 | | 100·00 | 100·00 | 100·0 |

This compound is isomeric with benzamic [amidobenzoic] and anthranilic acids.— ¶. It has usually been regarded as salicylamide, that is to say, as the neutral amide $N\left\{\begin{matrix}C^{14}H^5O^4\\H\\H\end{matrix}\right.$, of monobasic salicylic acid (pp. 249, 250). But Limpricht has shown that it forms definite salts with bases and may be regarded as an amidogen-acid formed from the type $\left.\begin{matrix}NH^4\\H\end{matrix}\right\}O^2$ by the substitution of the biatomic radical $C^{14}H^4O^2$, for 2 At. H in $NH^4$, its rational formula being therefore $\left.\begin{matrix}NH^2(C^{14}H^4O^2)\\H\end{matrix}\right\}O^2$.

*Decompositions.* 1. When heated considerably above its melting point, it begins to boil at 270°, giving off water and small quantities of secondary products (carbolic acid and carbonate of ammonia), and if the operation be stopped when one-fourth of the substance is volatilised, the residue consists of salicylimide, $C^{14}NH^5O^2 = C^{14}NH^7O^4 - 2HO$. (Limpricht.) ¶. — 2. Its vapour passed through a red-hot tube containing quick-lime, yields a very small quantity of aniline, together with large quantities of ammonia and carbolic acid. (Muspratt & Hofmann, *Ann. Pharm.* 53, 222.) — 3. Treated with fuming *nitric acid*, it yields a beautifully crystallised substitution-product. (Cahours.) — 4. It is decomposed by *chlorine* and *bromine*. — 4. Treated with strong bases and acids in excess, it is resolved into salicylic acid and ammonia. (Cahours.) [This statement requires modification (*v. inf.*)] — Dissolves without decomposition in hot hydrochloric and nitric acid, and is precipitated from the solutions by water. (Procter.) — 5. With chloride of benzoyl, it forms benzosalicylamide [benzosalicylamic acid] and hydrochloric acid. (Gerhardt & Chiozza.)

*Combinations.* The acid dissolves sparingly in cold, more abundantly in boiling *water*, and crystallises in long needles on cooling. (Procter, Cahours.) It dissolves readily in *potash-ley* and in *ammonia*. (Procter.) — ¶. It dissolves in aqueous solutions of the alkaline carbonates without elimination of carbonic acid, and crystallises out unaltered when the solutions are concentrated. It dissolves readily in warm aqueous ammonia and crystallises out unaltered as the ammonia evaporates. (Limpricht.)

The *Salicylamates* of *Potash* and *Soda* are obtained by decomposing the baryta-salt with an exactly equivalent quantity of sulphate of potash or soda; the liquid filtered from the sulphate of baryta and evaporated to a syrup, solidifies in a radiated crystalline mass difficult to purify. (Limpricht.)

*Salicylamate of Baryta.* — The acid dissolves readily in strong baryta-water and the solution yields by evaporation concentrically grouped needles of the baryta-salt, easily soluble in water.

*Salicylamate of Strontia.* — Prepared like the baryta-salt, which it much resembles.

| | *At* 100°. | | Limpricht. |
|---|---|---|---|
| Sr | 44 | 24·4 | 24·4 |
| $C^{14}NH^6O^4$ | 136 | 75·6 | 75·6 |
| $C^{14}NH^6SrO^4$ | 180 | 100·0 | 100·0 |

*Salicylamate of Lime.* — Obtained by treating the acid with milk of lime. — Very soluble crystals united in warty groups.

| | *At* 100°. | | Limpricht. |
|---|---|---|---|
| 14 C | 84 | 53·8 | |
| N | 14 | 9·0 | 8·8 |
| 6 H | 6 | 3·9 | |
| Ca | 20 | 12·8 | 12·4 |
| 4 O | 32 | 20·5 | |
| $C^{14}NH^6CaO^4$ | 156 | 100·0 | |

*Salicylamate of Magnesia.* — Obtained in warty, easily soluble crystals by digesting salicylamic acid with water and magnesia.

The solutions of the salicylamates of the alkaline earths appear to be decomposed during evaporation by the carbonic acid of the air. (Limpricht.)

*Salicylamate of Copper.* — Soluble salicylamates form with acetate of copper a green precipitate consisting of microscopic crystals.

| | *At* 100°. | | Limpricht. |
|---|---|---|---|
| 14 C | 84·0 | 50·1 | |
| N | 14·0 | 8·3 | 8·3 |
| 6 H | 6·0 | 3·6 | |
| Cu | 31·6 | 18·9 | 18·7 |
| 4 O | 32·0 | 19·1 | |
| $C^{14}NH^6CuO^4$ | 167·6 | 100·0 | |

*Salicylamate of Silver.* — Nitrate of silver added to the solution of an alkaline salicylamate, throws down grey amorphous flakes which blacken when the liquid is boiled.

| | *Dried over oil of vitriol.* | | Limpricht. |
|---|---|---|---|
| 14 C | 84 | 34·4 | |
| N | 14 | 5·7 | 5·4 |
| 6 H | 6 | 2·5 | |
| Ag | 108 | 44·3 | 44·3 |
| 4 O | 32 | 13·1 | |
| $C^{14}NH^6AgO^4$ | 244 | 100·0 | |

¶.

Salicylamic acid dissolves abundantly in *alcohol* and in *ether*.

## ¶. Salicylimide. $C^{14}NH^5O^2$.

LIMPRICHT. *Ann. Pharm.* 98, 261.

Produced by the action of heat on salicylamic acid (p. 321). The residue obtained by heating the acid to 270° is washed with cold alcohol, to remove undecomposed salicylamic acid; it then consists of a yellow powder, which under the microscope appears to consist of crystalline needles. Does not melt at 200°. It is coloured purple by sesquichloride of iron.

| | | | Limpricht. |
|---|---|---|---|
| 14 C | 84 | 70·6 | 70·3 |
| N | 14 | 11·8 | 11·7 |
| 5 H | 5 | 4·2 | 4·4 |
| 2 O | 16 | 13·4 | 13·6 |
| $C^{14}NH^5O^2$ | 119 | 100·0 | 100·0 |

May be regarded as $N\left\{\begin{matrix}C^{14}H^4O^2\\H\end{matrix}\right.$ that is to say as ammonia in which 2 H are replaced by the biatomic radical $C^{14}H^4O^2$. The formation of this compound affords decisive proof of the bibasic nature of salicylic acid.

Salicylimide is insoluble in water and in aqueous ammonia, but is dissolved by alcoholic ammonia, forming a yellow solution, which when evaporated leaves the compound apparently unaltered. Acids decolorise the solution; acetate of lead forms in it a white precipitate, nitrate of silver a yellowish precipitate, and sulphate of copper a slight greenish precipitate.

It is nearly insoluble in boiling alcohol and ether.

## ¶. Ethylsalicylamic Acid.

$$C^{18}NH^{11}O^4 = C^{14}(N.H.C^4H^5)H^5O^2\ [= \left.\begin{matrix}N.H.(C^4H^5)(C^{14}H^4O^2)\\H\end{matrix}\right\}O^2.]$$

LIMPRICHT. *Ann. Pharm.* 98, 262.

Obtained by the action of ammonia on methylsalicylate of ethyl (p. 258).

$$\left.\begin{matrix}C^{14}H^4O^2\\C^4H^5,C^2H^3\end{matrix}\right\}O^4 + NH^3 = \left.\begin{matrix}NH.(C^4H^5)(C^{14}H^4O^2)\\H\end{matrix}\right\}O^2 + C^2H^4O^2.$$

By the further action of ammonia, neutral salicylamide appears to be formed:

$$NH(C^4H^5)(C^{14}H^4O^2\left.\begin{matrix}\\H\end{matrix}\right\}O^2 + NH^3 = N^2\left\{\begin{matrix}C^{14}H^4O^2\\H^2,\ H^2\end{matrix}\right. + C^4H^6O^2.$$

Crystallises from the hot aqueous solution in small colourless needles; from alcohol or ether in somewhat thicker crystals. When immersed in a quantity of boiling water not sufficient to dissolve it, it melts into an oil; but when heated alone it melts only at 110°, and solidifies again in the crystalline form on cooling. Sublimes at a very moderate heat. Has a slight acid reaction.

| | | | Limpricht. a. | Limpricht. b. | Limpricht. c. |
|---|---|---|---|---|---|
| 18 C | 108 | 65·4 | 65·4 | 65·4 | 65·3 |
| N | 14 | 8·5 | 8·5 | 8·5 | |
| 11 H | 11 | 6·6 | 6·6 | 6·8 | 6·9 |
| 4 O | 32 | 19·5 | 19·5 | 19·3 | |
| $C^{18}NH^{11}O^4$ | 165 | 100·0 | 100·0 | 100·0 | |

*a* was prepared from methylsalicylate of ethyl obtained by heating methylsalicylate of baryta with sulphovinate of potash to 100° in sealed tubes; the oily neutral ether thus obtained was heated with aqueous ammonia to 100° in sealed tubes for a few hours; *b* and *c* were obtained by leaving aqueous ammonia in contact for some days at ordinary temperatures with methylsalicylate of ethyl prepared by heating methylsalicylate of potash with iodide of ethyl.

Ethylsalicylamic acid is nearly insoluble in cold water, but dissolves pretty readily in boiling *water*. The solution is coloured purple by sesquichloride of iron, green by sulphate of copper, and yields a precipitate with neutral acetate of lead after addition of ammonia.

It dissolves at a gentle heat in *hydrochloric, nitric* and strong *sulphuric acid*, and is precipitated from the two former on cooling, from the last on addition of water.

It dissolves in warm *potash-ley* and separates out on cooling.

In *alcohol* and *ether* it dissolves very readily at the boiling heat, much less at ordinary temperatures. ¶

## Benzoylsalicylamic Acid.

$$C^{28}NH^{11}O^6 = C^{14}(N.H.C^{14}H^5O^2)H^5O^2,O^2\left[=\left.\begin{matrix}N.H.(C^{14}H^5O^2)(C^{14}H^4O^2)\\H\end{matrix}\right\}O^2.\right.$$

GERHARDT & CHIOZZA. *Compt. rend.* 37, 86.
LIMPRICHT. *Ann. Pharm.* 99, 249.

*Benzoylsalicylamid, Azoture de benzoïle, de salicyle et d'hydrogène.*

*Formation.* By the action of chloride of benzoyl on salicylamic acid:

$$C^{14}NH^7O^4 + C^{14}ClH^5O^2 = C^{28}NH^{11}O^6 + HCl.$$

*Preparation.* Chloride of benzoyl and salicylamic acid in equal numbers of atoms are heated together to 120° — 145° as long as hydrochloric acid continues to escape; and the residue — which remains liquid and viscid for a long time after cooling, but becomes crystalline on the addition of a few drops of alcohol or ether — is washed with a small quantity of ether and dissolved in boiling alcohol, whence it crystallises on cooling.

Very slender needles united in flocks.

The acid when heated gives off water and is converted into benzoylsalicylimide (Limpricht):

$$C^{28}NH^{11}O^6 - 2HO = C^{28}NH^9O^4.$$

After fusion it remains for a long time resinous and gummy, and is no longer completely soluble in hot ammonia. The yellow residue dissolves easily in alcohol, and the yellow solution deposits after evaporation small needles which dissolve very readily in alcohol, forming a yellow solution which is decolorised by hydrochloric acid; they appear to consist of an ammonia-salt. — It is attacked by chloride of benzoyl, and the crystalline product appears to be reconverted into benzoylsalicylamic acid by the action of water or alcohol. (Gerhardt & Chiozza.)

The acid dissolves very easily in ammonia, but is deposited in its original state when the ammonia evaporates (Gerhardt & Chiozza, Limpricht), or when the solution is mixed with an acid. (Limpricht.) The acid dissolves in the fixed alkalis, forming deep yellow solutions, but is generally resolved at the same time into benzoic and salicylamic acids. (Limpricht.) — It dissolves in warm carbonate of soda without evolution of carbonic acid; and the solution when treated with acids, deposits very soluble crystals, probably consisting of benzoic and salicylamic acids. (Limpricht.) — Its solution in strontia-water first deposits crystals of benzoate and afterwards of salicylamate of strontia. The first crop of crystals contained 26·6 p. c. strontium, and the second 24·4 p. c.; the formula of the benzoate requires 26·4 p. c., and that of the salicylamate 23·3 p. c. strontium. (Limpricht.)

The ammoniacal solution forms a light lemon-yellow precipitate with neutral acetate of lead, and light blue with sulphate of copper. (Gerhardt & Chiozza.)

*Silver-salt.* — The ammoniacal solution of the acid forms with nitrate of silver a yellow precipitate which becomes strongly heated with chloride of benzoyl, forming chloride of silver. (Gerhardt & Chiozza.)

| | | | Limpricht. |
|---|---|---|---|
| $C^{28}NH^{10}O^{6}$ | 240 | 69 | |
| Ag | 108 | 31 | 30 |
| $C^{28}NH^{10}AgO^{6}$ | 348 | 100 | |

The acid dissolves very sparingly in boiling alchohol.

## ¶ Benzoylsalicylimide.

$C^{28}NH^{9}O^{4} = N.C^{14}H^{5}O^{2},C^{14}H^{4}O^{2}$.

LIMPRICHT. *Ann. Pharm.* 99, 250.

Benzoylsalicylamic acid heated to 270° in a small retort till about one-third has volatilised, yields a distillate containing water, benzoic acid and oily products, and a residue consisting of benzoylsalicylimide and undecomposed benzoylsalicylamic acid, which latter may be removed by boiling with small quantities of alcohol. The remaining pulverulent benzoylsalicylimide dissolved in a larger quantity of boiling alcohol, separates on cooling in small yellowish needles, which when dry form a slightly interlaced mass.

| | | | | Limpricht. |
|---|---|---|---|---|
| 28 C | 168 | 75·3 | 76·1 | 75·2 |
| N | 14 | 6·3 | | |
| 9 H | 9 | 4·0 | 5·0 | 4·8 |
| 4 O | 32 | 14·4 | | |
| $C^{28}NH^9O^4$ | 223 | 100·0 | | |

Ammonia in which 2 At. H are replaced by $C^{14}H^4O^2$, and the remaining atom by benzoyl $C^{14}H^5O^2$.

The compound dissolves in about 1000 pts. of boiling *alcohol*. ¶.

## Anthranilic Acid.

$C^{14}NH^7O^4 = C^{14}AdH^5O^2O^2$.

FRITZSCHE. (1841.) *J. pr. Chem.* 23, 76; *Ann. Pharm.* 39, 83; *Pharm. Centr.* 1841, 327.
LIEBIG. *Ann. Pharm.* 39, 91; *Pharm. Centr.* 1841, 601.
CHANCEL. *Compt. chim.* 1849, 185; *Compt. rend.* 28, 422; *Pharm. Centr.* 1849, 332.
GERLAND. *Ann. Pharm.* 86, 143; abstr. *J. pr. Chem.* 57, 252; 60, 110; *Chem Gaz.* 1852, 237; *Pharm. Centr.* 1853, 801.
KUBEL. *Ann. Pharm.* 102, 236.

***Carbanilic acid, Phenylcarbamic acid.***

*Formation.* 1. By heating indigo with potash-ley. (Fritzsche.) — 2. By heating chrysanilic acid with dilute acids. (Fritzsche.) — 3. By the action of potash on aniline-urea. (Chancel.)

$$C^{14}N^2H^5O^2 + KO,HO = C^{14}NH^6KO^4 + NH^3.$$

*Preparation.* 1. Indigo from the vat is added in small portions to boiling potash-ley of such a strength as to boil at 150°, till chrysanilate of potash begins to separate; the mass which solidifies on cooling is dissolved in alcohol and filtered; the filtrate is exposed to the air till its green colour changes to brown; the caustic potash converted into carbonate by passing carbonic acid into it; and the liquid decanted from this salt is freed from alcohol by distillation: as the solution becomes concentrated, anthranilate of potash separates out. The saline mass freed from the mother-liquor by means of bibulous paper is dissolved in the smallest possible quantity of water; and the filtered solution is mixed with acetic acid, which at first produces turbidity and afterwards an abundant crystalline precipitate of anthranilic acid. The acid first separates in small drops which afterwards unite into crystals. (Fritzsche.) — 2. When chrysanilic acid is boiled for some time with dilute sulphuric acid, the solution on cooling deposits black-blue needles; and the liquid separated therefrom containing anthranilic acid and another acid, is saturated with sulphate of zinc, and carefully neutralised with dilute potash, whereby anthranilate of zinc is precipitated in the form of a fine yellowish powder difficult to wash. If a small brownish flocculent precipitate forms at the beginning of the neutralisation, the liquid must be filtered from this precipitate before the zinc-salt is further neutralised with potash. The zinc-salt is heated with alcohol to the boiling point; sulphuric acid diluted with alcohol is added by drops, avoiding an

excess; and the liquid is filtered: anthranilic acid then separates from it either on cooling or after partial evaporation. (Fritzsche.)—3. One pt. of finely pulverised indigo boiled in a silver dish with 10 pts. of potash-ley of sp. gr. 1·35, is quickly attacked, without evolution of gas. The solution, which becomes red and thickish, is repeatedly diluted with water and then concentrated by boiling; and before all the indigo is dissolved, peroxide of manganese is added in successive small portions till a sample diluted with water no longer turns blue on exposure to the air. The thick mass, which now contains nothing but anthranilate of potash and a little free potash, is diluted with hot water, and supersaturated with dilute sulphuric acid; the resulting grey-brown precipitate separated by filtration; the filtrate neutralised with potash and evaporated to dryness; and the anthranilate of potash extracted from the residue by cold water or alcohol. The aqueous solution (obtained by treating with water the residue of the alcoholic solution, if alcohol has been used as the solvent) mixed with acetic acid, yields after 24 hours an abundant crystallisation of anthranilic acid. These crystals are washed with warm water, dissolved in 10 to 15 pts. of boiling water, and milk of lime then added sufficient to produce an alkaline reaction; the liquid filtered from the excess of lime yields on cooling colourless crystals of anthranilate of lime. If coloured, they must be decolorised by solution in hot water and boiling with animal charcoal. The hot aqueous solution of the lime-salt mixed with acetic acid, deposits the acid in yellowish crystals as it cools. If the crystallisation is preceded by a milky turbidity, there is an impurity present which must be removed by boiling with blood-charcoal. (Liebig.)

4. Aniline-urea is boiled with strong potash-ley as long as ammonia continues to escape, and the liquid is supersaturated with acetic acid. If the solution has not been too much concentrated, no precipitate appears, but the anthranilic acid separates on cooling in crystals which may be purified by recrystallisation. (Chancel.)

*Properties.* Transparent, very lustrous laminæ with dihedral summits.—The nearly cooled solution of the lime-salt yields, after addition of acetic acid, slender white four and six-sided needles. (Liebig.) The acid obtained by the first process (p. 326) is a sandy powder; if the acetic acid forms a layer above the other liquid, colourless crystalline scales are obtained, resembling those of benzoic acid; the alcoholic solution yields large crystalline laminæ. (Fritzsche.) The acid melts at about 135°. (Fritzsche.) It sublimes at a gentle heat in shining laminæ resembling those of sublimed benzoic acid (Liebig); as a fine crystalline powder. (Fritzsche.) Has a sweetish taste. (Fritzsche.)

| | | | Fritzsche. | Liebig. |
|---|---|---|---|---|
| 14 C | 84 | 61·23 | 61·08 | 61·13 |
| N | 14 | 10·22 | 10·95 | |
| 7 H | 7 | 5·11 | 4·97 | 5·16 |
| 4 O | 32 | 23·44 | 23·00 | |
| $C^{14}NH^7O^4$ | 137 | 100·00 | 100·00 | |

Isomeric with amidobenzoic and salicylamic acids.

*Decompositions.* 1. Boils when heated above 135° and is resolved into carbonic acid and aniline. (Fritzsche.)

$$C^{14}NH^7O^4 = C^{12}NH^7 + 2CO^2.$$

The decomposition is most complete when the acid is mixed with twice its bulk of powdered glass and distilled in a glass tube over a spirit-lamp; the distillate yields laminæ of anthranilic acid which disappear in rectification. (Liebig.) — 2. Heated with ordinary *nitric acid*, it does not evolve any nitrous vapours, and the liquid on cooling deposits crystalline laminæ which dissolve readily in water, do not precipitate baryta-water, colour ferric salts blood-red, and give off ammonia when treated with potash: they are therefore nitrosalicylate of ammonia. (Gerhardt, *N. Ann. Chim. Phys.* 7, 227.) — 3. When nitrous acid is passed into the dilute aqueous solution of anthranilic acid, as long as bubbles of nitrogen are evolved, it is resolved into salicylic acid, nitrogen and water. (Gerhardt.)

$$C^{14}NH^7O^4 + NO^3 = C^{14}H^6O^6 + 2N + HO.$$

4. The acid treated with chlorate of potash and hydrochloric acid yields chloranil (Hofmann, *Ann. Pharm.* 52, 65):

$$C^{14}NH^7O^4 + 8Cl + 4O = C^{12}Cl^4O^4 + 2CO^2 + 4Cl + NH^3.$$

*Combinations.* The acid dissolves with some difficulty in cold but pretty easily in boiling *water*.

¶. *Sulphate of Anthranilic Acid.* — $C^{14}NH^7O^4,SHO^4$. — Obtained by precipitating the hydrochlorate with sulphate of silver. Generally forms needles united in concentric groups. (Kubel.)

| | | | | Kubel. |
|---|---|---|---|---|
| $C^{14}NH^7O^4$ | 137 | 73·66 | | |
| $SHO^4$ | 49 | 26·24 | | 26·26 |
| $C^{14}NH^7O^4,SHO^4$ | 186 | 100·00 | | |

*Hydrochlorate.* $C^{14}NH^7O^4,HCl$. — Dry anthranilic acid prepared from indigo absorbs hydrochloric acid gas, but does not in this manner readily form a definite compound. But when anthranilic acid is dissolved in warm concentrated hydrochloric acid, the new compound crystallises in slender needles on cooling. (Kubel.)

| *Dried over oil of vitriol.* | | | | Kubel. |
|---|---|---|---|---|
| $C^{14}NH^7O^4$ | 137·0 | 79·46 | | |
| HCl | 35·4 | 20·54 | | 20·96 |
| $C^{14}NH^7O^4,HCl$ | 172·4 | 100·00 | | |

*Nitrate.* $C^{14}NH^7O^4,NHO^6$. — Obtained by precipitating the hydrochlorate with 1 At. nitrate of silver. The liquid filtered from the chloride of silver yields by evaporation large prismatic crystals easily soluble in boiling alcohol. — When 1 At. of hydrochlorate of anthranilic acid is mixed with 2 At. nitrate of silver, the filtered liquid after concentration yields a compound which contains silver, but apparently not in sufficient quantity to form the compound $C^{14}NH^7O^4,NHO^6 + NAgO^6$ — Nitrate of baryta does not appear to combine with nitrate of anthranilic acid. (Kubel.)

*Oxalate.* — Prepared by treating the hydrochlorate with oxalate of silver. Crystallises in small silky scales. (Kubel.)

| | At 100°. | | Kubel. |
|---|---|---|---|
| 2 $C^{14}NH^7O^4$ | 274 | 75·27 | |
| $C^4H^2O^8$ | 90 | 24·73 | 26·25 |
| $(C^{14}NH^7O^4)^2,C^4H^2O^8$ | 364 | 100·00 | ¶. |

The compounds of anthranilic acid with bases yield aniline by dry distillation, like the free acid, but a considerable quantity of charcoal is separated at the same time. The decomposition is less simple than that of the free acid, because in the salts, one atom of hydrogen is replaced by a metal. (Fritzsche.)

The anthranilates of the *alkalis* are crystallisable, dissolve readily in water and alcohol, have a sweetish taste, and do not deliquesce when exposed to the air. (Fritzsche.)

*Anthranilate of Lime* crystallises from the hot aqueous solution in colourless transparent rhombohedrons; it dissolves sparingly in cold, but with tolerable facility in hot water. (Liebig.)

*Anthranilate of Silver.* — The solution of the lime-salt, or the aqueous acid neutralised with ammonia, yields, when mixed at the boiling heat with nitrate of silver, a precipitate composed of white laminæ, which dissolves completely in boiling water and crystallises with silvery lustre on cooling. (Liebig.)

| | | | Liebig. |
|---|---|---|---|
| 14 C | 84·0 | 34·41 | 34·19 |
| N | 14·0 | 5·73 | |
| 6 H | 6·0 | 2·46 | 2·45 |
| Ag | 108·1 | 44·28 | 43·96 |
| 4 O | 32·0 | 13·12 | |
| $C^{14}NH^6AgO^4$ | 244·1 | 100·00 | |

The acid dissolves readily in *alcohol* and *ether*.

*Appendix to Anthranilic Acid.*

## Chrysanilic Acid.

FRITZSCHE. (1841.) *J. pr. Chem.* 23, 67; *Ann. Pharm.* 39, 78. — *J. pr. Chem.* 28, 199; *Pharm. Centr.* 1841, 323.
GERHARDT. *Rev. scientif.* 10, 371.

*Preparation.* Finely divided indigo is added by successive portions to potash-ley boiling at 150°, till chrysanilate of potash begins to separate, the mixture is then left to cool, and water added to the solidified mass. The liquid is either mixed with a quantity of dilute acid sufficient only to saturate the greater part of the potash; the bluish green precipitate separated by filtration; and the chrysanilic acid precipitated from the golden yellow liquid by addition of excess of acid;—or the solution of chrysanilate of potash is immediately supersaturated with very dilute acid; the precipitate of impure chrysanilic acid thrown into a large quantity of water; potash-solution then added by drops as long as the solution retains its pure gold-yellow colour; and the liquid immediately

filtered into an excess of dilute acid. (If too much potash-solution is used, the liquid immediately acquires a greenish tint) a portion of the impurities being then redissolved, and a decomposition takes place in the liquid, a thin film of indigo-blue forming on the surface; but by careful neutralisation with dilute acid, the pure gold-yellow colour may be restored. After the precipitate has been thrown on the filter, the last portions of liquid must be allowed to drain off before the precipitate is washed with water, because the residue is partially dissolved by pure water, and consequently the wash-water does not yield a perfectly pure acid by precipitation.) — The chrysanilic acid obtained by precipitation is purified by solution in a boiling mixture of equal parts of alcohol and water, which deposits it in the crystalline form on cooling.

*Properties.* Microscopic needles united in dense stellate groups; by precipitation, red-brown flakes resembling kermes are obtained, lighter in colour the greater the excess of acid added, but becoming darker by washing with water, and dark brown-red or sometimes dark green when dry.

According to Fritzsche, the acid contains in 100 pts.:

| | *a.* | *b.* | *c.* | *d.* | *e.* | *f.* |
|---|---|---|---|---|---|---|
| C | 65·74 | 66·03 | 66·74 | 68·62 | 68·74 | 69·06 |
| H | 4·34 | 4·23 | 4·46 | 4·27 | 4·38 | 4·33 |

*a*, *b* and *c* were obtained by precipitation; *d*, *e* and *f* were purified by solution in alcohol. According to Gerhardt, chrysanilic acid is a mixture of isatic acid or isatin with more or less reduced indigo (*Rev. scient.* 10, 371).

*Decompositions.* Boiled with dilute mineral acids, it forms a brown red solution continually becoming deeper in colour, and is completely resolved into anthranilic acid and an indifferent substance, which on cooling separates almost completely in slender blue-black needles. These crystals when recently formed dissolve in alcohol, forming a deep red-purple solution with a tinge of blue; but after drying, they form with cold alcohol, a red solution, leaving on the filter an indigo-coloured substance which forms a violet solution with cold alcohol or ether, dissolves somewhat more abundantly in boiling alcohol, and crystallises on cooling in black blue scales not exhibiting any coppery lustre. After drying, the black-blue needles dissolve less easily and with red-brown colour; both solutions appear to be altered by exposure to the air. In the fresh and still moist state, they are quickly decomposed by alkalis, with separation of indigo; after drying, they decompose slowly. They contain in 100 parts

| | *a.* | *b.* | *c.* |
|---|---|---|---|
| C | 66·85 | 72·55 | 73·89 |
| H | 3·95 | 3·97 | 3·96 |

*a* was prepared from chrysanilic acid obtained by precipitation; *b* and *c* from chrysanilic acid purified by solution in hot alcohol. — When chrysanilic acid is boiled with alcohol to which a few drops of sulphuric or hydrochloric acid are added, a red-brown solution is formed, which by cooling or by evaporation at a gentle heat, deposits a red-brown crystalline product. A hot alcoholic solution of chrysanilate of ammonia supersaturated with hydrochloric acid deposits on cooling long very slender needles. (Fritzsche.)

2. Recently precipitated chrysanilic acid forms with excess of concentrated ammonia, a greenish yellow crystalline product, which does not evolve ammonia when treated with cold solution of potash. The aqueous or alcoholic solution of this substance mixed with hydrochloric acid, and left to evaporate, deposits yellow-green needles; frequently however—*e.g.* after heating or continued contact with the air—blue flakes are deposited, either instead of these needles or together with them. With nitrate of silver, the solution forms a precipitate consisting of interlaced microscopic needles, a separation of metallic silver occasionally taking place at the same time. (Fritzsche.)

3. The solution of an alkaline chrysanilate exposed to the air becomes covered with a light-green film which appears crystalline under the microscope, and yields small crystals when dissolved in ether.

4. A solution of chrysanilic acid mixed with nitrate of silver forms at first an orange-yellow precipitate (probably chrysanilate of silver), which however soon assumes a dark-brown red colour, and after addition of a little nitric acid, changes into a heavy grey precipitate containing a large quantity of metallic silver, whilst the liquid retains in solution a silver-salt which separates in flesh-coloured flakes when the liquid is neutralised with ammonia. From the heavy grey precipitate alcohol extracts the substance obtained in the preceding reaction (3); it has more or less of a dark green colour, arising merely from impurities, since when heated with nitric acid, it assumes a lemon-yellow colour, without being much attacked.

*Combinations.* Chrysanilic acid dissolves very sparingly in water, forming a yellowish solution. It dissolves with gold-yellow colour in alkalis, but is readily decomposed by excess of alkali.

*Chrysanilate of Ammonia* is obtained pure only when alcoholic solutions are employed.

*Chrysanilate of Potash* forms small yellow crystals easily soluble in water. With metallic salts, it forms precipitates of various colours.

*Chrysanilate of Zinc.*—Obtained by adding a solution of the potash or ammonia-salt, as nearly neutral as possible, to a boiling solution of acetate of zinc mixed with acetic acid. Powder of a fine brick-red colour, which settles down quickly, and appears crystalline under the microscope. By analysis it is found to contain sometimes 14 At., sometimes 42 At. carbon to 1 At. zinc-oxide.

*Chrysanilate of Lead.*—Obtained like the zinc-salt and exhibits similar properties. Its composition agrees nearly with the formula $C^{28}H^{10}N^{2}O^{5},PbO$.

Chrysanilic acid dissolves readily in *alcohol*, forming a reddish yellow solution.

---

## Salicyluric Acid.

$C^{18}NH^{9}O^{6} = C^{16}AdH^{7}O^{6}$.

C. Bertagnini. (1855.) *Nuovo Cimento.* 1, 363.

Occurs in the urine after salicylic acid has been swallowed.

*Preparation.* The acid urine voided after taking salicylic acid is evaporated down to 12° Bm., acidulated with hydrochloric acid, shaken up with ether and the ether distilled from the ethereal solution. The residue yields by spontaneous evaporation, large crystalline nodules, which, when freed from the mother-liquor by pressure, dissolved in boiling water, and treated with animal charcoal, yield a crystalline mass consisting for the most part of slender needles, mixed with larger needles of salicylic acid. On heating this mixture in a current of air to between 140° and 150°, the salicylic acid volatilises, and the residue crystallised from hot water containing animal charcoal yields pure salicyluric acid.

*Properties.* Slender, shining, crystalline needles, which when obtained from the aqueous solution are grouped concentrically. Has a somewhat bitter taste and a strong acid reaction. Melts at about 160°, and solidifies in the crystalline form. The solutions colour ferric salts violet like salicylic acid.

| | | | Bertagnini. |
|---|---|---|---|
| 18 C | 108 | 55·38 | 55·67 |
| N | 14 | 7·18 | 7·44 |
| 9 H | 9 | 4·62 | 4·81 |
| 8 O | 64 | 32·82 | 32·08 |
| $C^{18}NH^{9}O^{8}$ | 195 | 100·00 | 100·00 |

Related to salicylic acid in the same manner as hippuric to benzoic acid.

*Decompositions.* 1. Between 160° and 170°, the acid turns brown and begins to decompose, yielding a sublimate of salicylic acid. At a stronger heat, it swells up and gives off ammonia, leaving a residue of charcoal. — 2. When boiled with excess of baryta-water, it does not form any salicylate of baryta; a small quantity of ammonia is however given off. — 3. Heated for a short time with fuming hydrochloric acid, it dissolves and crystallises out again unaltered; but if the boiling be continued for two or three hours, the acid is resolved into salicylic acid and glycocol.

$$C^{18}NH^{9}O^{8} + 2HO = C^{14}H^{6}O^{6} + C^{4}NH^{5}O^{4}.$$

4. When it is boiled with water and peroxide of lead, the latter is decolorised, and on boiling, the solution, small shining needles separate out.

*Combinations.* The acid dissolves readily in boiling *water*, less in cold water.

The *salicylurates* crystallise with facility. The acid expels carbonic acid from its compounds.

*Salicylurate of Baryta.* — Obtained by dissolving carbonate of baryta in the warm acid. As the solution cools, the salt crystallises in large hard prisms, which become opaque and give off water when heated, then melt and decompose, giving off ammonia and an oil which smells like hydrate of phenyl, and leaving a residue of carbonate of baryta. The salt is sparingly soluble in cold water.

*Salicylurate of Lime.* — *a.* When carbonate of lime is dissolved in the aqueous acid, the solution on cooling yields aggregated needles which are sparingly soluble in cold water and insoluble in alcohol.

*b.* When milk of lime is added by successive small quantities to the warm aqueous acid, a solution is at first obtained which suddenly solidifies in a crystalline mass insoluble in boiling water.

The acid dissolves readily in *alcohol* and with tolerable facility in *ether*.

*Nitro-oxyamidogen Nucleus* $C^{14}AdXH^4O^2$.

## Nitrosalicylamic Acid.

$C^{14}N^2H^6O^6 = C^{14}AdXH^4O^2,O^2$.

CAHOURS. *N. Ann. Chim. Phys.* 10, 352; *Pharm. Centr.* 1844, 439.

*Nitrosalicylamide, Anilamide.*

Methylnitrosalicylic acid left for three weeks in a warm place in contact with strong ammonia, gradually disappears and yields a yellowish red liquid, which, when evaporated at a gentle heat, deposits a bright red mass easily soluble in water especially if it contains ammonia, and precipitated therefrom by acid in yellow flakes; and on dissolving these in alcohol after they have been washed with water, and evaporating the solution, the acid separates in yellow shining crystals. — May be partially volatilised without decomposition.

| | | | Cahours. |
|---|---|---|---|
| 14 C | 84 | 46·15 | 45·90 |
| 2 N | 28 | 15·38 | 15·31 |
| 6 H | 6 | 3·29 | 3·44 |
| 8 O | 64 | 35·18 | 35·35 |
| $C^{14}N^2H^6O^8$ | 182 | 100·00 | 100·00 |

Boiled with potash-ley, it gives off ammonia, and forms nitrosalicylate of potash.

It is nearly insoluble in cold *water*, but colours it nevertheless. In boiling water it is much more soluble.

It dissolves readily in cold *ammonia, potash* or *soda*, and is precipitated therefrom by acids in its original state.

It dissolves readily in *alcohol* and *ether*.

*Azo nucleus* $C^{14}NH^7$.

## Toluidine.

$C^{14}NH^9 = C^{14}NH^7,H^2$.

MUSPRATT & HOFMANN. (1845.) *Ann. Pharm.* 54, 1; *Pharm. Centr.* 1848, 513.

NOAD. *Ann. Pharm.* 63, 305; *Pharm. Centr.* 1848, 182.

A. W. HOFMANN. *Ann. Pharm.* 66, 144; *Pharm. Centr.* 1848, 582.

WILSON. *Ann. Pharm.* 77, 216; *Chem. Soc. Qu. J.* 3, 154; *Pharm. Centr.* 1851, 110.

CHAUTARD. *N. J. Pharm.*. 24, 166; *J. pr. Chem.* 60, 240.

*Formation.* 1. When nitrotoluol is decomposed by sulphuretted hydrogen in presence of ammonia or potash. (Muspratt & Hofmann, Wilson.)—2. By the action of potash on the yellow mixture of resin obtained by treating oil of turpentine with nitric acid. (Chautard.)

*Preparation.* Nitrotoluol is dissolved in alcohol saturated with ammonia, and sulphuretted hydrogen passed into the liquid till its odour no longer disappears even after long standing; sulphur then separates in fine crystals. To accelerate the decomposition, the liquid saturated with sulphuretted hydrogen is heated in a retort to the boiling point, whereupon a large quantity of sulphuretted hydrogen is evolved; the distillate is then poured back, the liquid again saturated with sulphuretted hydrogen, and these operations repeated five or six times. The liquid is now mixed with water and excess of hydrochloric acid and shaken up with ether (which still takes up a certain quantity of undecomposed nitrotoluol, even after long treatment with sulphuretted hydrogen); and the alcoholic liquid is evaporated down to one-third to expel the alcohol, and distilled with potash, whereupon ammonia and toluidine pass over with the water, the toluidine collecting at the bottom in the form of a heavy oil which crystallises after a while. The entire distillate is supersaturated with oxalic acid and evaporated to dryness over the water-bath; the residual mixture of oxalate of ammonia and oxalate of toluidine boiled with absolute alcohol, which dissolves only the oxalate of toluidine and deposits it in slender white needles on cooling. These crystals are dissolved in hot water, and the solution is mixed with strong potash-ley; the toluidine then separates immediately in oily drops which rise to the surface, and collect into a film of liquid which crystallises with a radiating structure on cooling. The crystalline crust is washed with cold water till it no longer imparts to the water an alkaline reaction; then pressed between paper, and rectified by one distillation (Muspratt & Hofmann); or it is dissolved in ether and the solution left to evaporate slowly. (Noad.)—The complete conversion of nitrotoluol into toluidine by hydrosulphate of ammonia is difficult. With hydrosulphate of potash only half the time is required and no separation of ammonia. The oxalate merely requires to be several times recrystallised and distilled with baryta. (Wilson.)

2. Potash-solution is gradually added to the yellow resinous mixture produced by the action of nitric acid on oil of turpentine (if the quantity is large, it is best to make the mixture in a retort provided with an S-shaped funnel-tube). The mixture then assumes a dark red-brown colour, becomes very hot, swells up, and yields an alkaline distillate smelling like ammonia and phosphuretted hydrogen. As soon as the spontaneous ebullition has ceased, the mixture is heated till it no longer smells distinctly of ammonia. The distillate is supersaturated with hydrochloric acid, whereby resinous matters are separated, then evaporated to dryness over the water-bath, and treated with absolute alcohol which leaves sal-ammoniac and dissolves hydrochlorate of toluidine. (Chautard.)

*Properties.* Crystallises from solution in hydrated alcohol saturated while hot, in large broad colourless laminæ. Melts at 40° into a colourless, strongly refracting oil. Evaporates at ordinary temperatures and forms white clouds with hydrochloric acid held over it (less with nitric acid). Forms on paper a grease-spot which soon disappears. Boils at 198°. Has a vinous aromatic odour (just like that of aniline), and a burning taste. Blues litmus slightly, changes the colouring matter of

dahlias to green, but does not redden turmeric. Colours fir-wood deep yellow. Does not produce a violet-blue colour with chloride of lime.

| | | | Muspratt & Hofmann. |
|---|---|---|---|
| 14 C | 84 | 78·51 | 78·53 |
| N | 14 | 13·08 | |
| 9 H | 9 | 8·41 | 8·61 |
| $C^{14}NH^{9}$ | 107 | 100·00 | |

*Decompositions.* 1. Toluidine on which bromine is poured becomes strongly heated and evolves copious fumes of hydrobromic acid; when the resulting mass is heated, white shining needles sublime, consisting of a bromine-compound which is no longer basic, very much resembles terbromaniline, and is insoluble in water, but soluble in alcohol and ether. — 2. With aqueous chloride of lime it acquires only a faint reddish tint. — 3. Nitric acid colours it deep red. When boiled with strong nitric acid, it is decomposed, with violent evolution of nitrous acid; water added to the solution throws down sulphur-yellow flakes, which dissolve in alkalis with brown-red colour, and are reprecipitated therefrom by acids. (Muspratt & Hofmann.) — 4. Toluidine is not set on fire by chromic acid. With aqueous chromic acid, it forms a red-brown precipitate which appears to be chromate of toluidine. — 5. Vapour of toluidine passed over melting potassium forms cyanide of potassium with vivid combustion.

6. An alcoholic solution of toluidine through which cyanogen gas is passed behaves like that of aniline (xi, 253; vid. *Cyanotoluidine.*) (Hofmann.) — 7. Toluidine over which the vapour of volatile chloride of cyanogen is passed, is converted into hydrochlorate of metoluidine. (Wilson.)

$$2C^{14}NH^{9} + C^{2}NCl = C^{30}N^{3}H^{17} + HCl.$$

8. Heated with bromide or iodide of ethyl, it forms ethyltoluidine. (Hofmann.)

9. With *anilocyanic acid* it forms a solid crystalline mass, corresponding with carbamide and carbanilide. (Hofmann.)

*Combinations.* Toluidine dissolves sparingly in cold, more readily in warm water, whence it is gradually deposited in iridescent laminæ on cooling. It dissolves readily in bisulphide of carbon. (Muspratt & Hofmann.)

Toluidine precipitates ferric salts. The *salts of Toluidine* are decomposed by ammonia, potash and soda and their carbonates, toluidine being separated in the form of a crystalline curd. They have a great tendency to crystallise; an alcoholic solution of toluidine solidifies with most acids in crystalline masses which yield beautiful crystals when recrystallised from water or alcohol. They are inodorous and colourless (excepting the gold, platinum and palladium double salts) but quickly become rose-coloured on exposure to the air. Their acid solutions impart a deep yellow colour to fir-wood and elder-pith.

The *Phosphate* and *Sulphite of Toluidine* are crystallisable.

*Sulphate of Toluidine.* — An ethereal solution of toluidine to which a few drops of sulphuric acid are added, immediately forms a snow-white crystalline precipitate, which may be washed with ether. — Easily soluble in water, sparingly in alcohol. (Muspratt & Hofmann.)

| | | | | Muspratt & Hofmann. |
|---|---|---|---|---|
| $C^{14}NH^9$ | 107 | 68·59 | | |
| HO | 9 | 5·77 | | |
| $SO^3$ | 40 | 25·64 | | 25·22 |
| $C^{14}NH^9,HO,SO^3$ | 156 | 100·00 | | |

*Hydrochlorate of Toluidine.* — The solution of toluidine in hydrochloric acid yields when evaporated and cooled, white crystalline scales, which quickly assume a yellow colour in contact with the air, and sublime like sal-ammoniac. It dissolves readily in water and alcohol, sparingly in ether. The solution has an acid reaction. (Muspratt & Hofmann.)

| | | | Muspratt & Hofmann. |
|---|---|---|---|
| $C^{14}NH^9$ | 107·0 | 74·62 | |
| ClH | 36·4 | 25·38 | 25·29 |
| $C^{14}NH^9,ClH$ | 143·4 | 100·00 | |

*Nitrate of Toluidine* is crystallisable.

Toluidine forms with *chromic acid* a red-brown precipitate, which appears to be chromate of toluidine.

Toluidine forms with *cupric* sulphate or chloride, a greenish, somewhat crystalline precipitate, and with *nitrate of silver*, a white precipitate which soon blackens, and must be a double salt. (Muspratt & Hofmann.)

*Chloro-aurate of Toluidine.* — Hydrochlorate of toluidine forms with chloride of gold a thick precipitate, which soon aggregates into an interlaced crystalline mass. Melts in water between 50° and 60°, and dissolves in rather hot water, separating in splendid yellow needles as the liquid cools. (Chautard.)

| | | | |
|---|---|---|---|
| 14 C | 84·0 | 18·82 | 19·71 |
| N | 14·0 | 3·14 | 3·42 |
| 10 H | 10·0 | 2·24 | 2·35 |
| Au | 196·6 | 44·06 | 43·26 |
| 4 Cl | 141·6 | 31·74 | 31·87 |
| $C^{14}NH^{10}Cl,AuCl^3$ | 446·2 | 100·00 | 100·61 |

*Chloroplatinate of Toluidine.* — Hydrochlorate of toluidine mixed with bichloride of platinum solidifies into an orange-yellow pulp of crystalline spangles, which may be washed with a mixture of ether and alcohol and dried in the water-bath. (Muspratt & Hofmann.) Contains 31·36 p. c. of platinum (Muspratt & Hofmann), 31·4 p. c. (Noad), and is therefore $C^{14}NH^{10}Cl,PtCl^2$.

*Chloropalladiate of Toluidine.* — Orange-yellow precipitate resembling the platinum-salt, but somewhat paler. (Muspratt & Hofmann.)

*Oxalate of Toluidine.* — An alcoholic solution of toluidine mixed with oxalic acid forms delicate silky needles, which dissolve sparingly in cold, more readily in boiling water or alcohol, and are insoluble in ether. The solution has a strong acid reaction and a saline taste, with unpleasant burning aftertaste. Contains 34·33 p. c. hypoth. anhydrous oxalic acid. (Muspratt & Hofmann.)

| | | | | Muspratt & Hofmann. |
|---|---|---|---|---|
| 18 C | 108 | .... | 52·43 | ..... 51·99 |
| N | 14 | .... | 6·79 | |
| 12 H | 12 | .... | 5·83 | ..... 5·90 |
| 9 O | 72 | .... | 34·95 | |
| $C^{14}NH^9,C^4H^2O^6$ + Aq | 206 | .... | 100·00 | |

Toluidine dissolves in *wood-spirit, alcohol,* and *ether;* ether abstracts it from the aqueous solution. It dissolves in *acetone,* and in *oils* both *fixed* and *volatile.* (Muspratt & Hofmann.)

## Lutidine.

$C^{14}NH^9 = C^{14}AdH^5,H^3$. ?

ANDERSON. (1851.) *Phil. Mag. J.* [4], 2, 457; *Ann. Pharm.* 80, 44; *J. pr. Chem.* 54, 36; *Pharm. Centr.* 1851, 914.

C. GREVILLE WILLIAMS. *Chem. Soc. Qu. J.* 7, 97.—*Phil. Mag. J.* [4], 8, 209.—*Edinb. Phil. Trans.* 21, Pt. ii.; *N. Ann. Chim. Phys.* 45, 488.

*Formation.* By the dry distillation of bones (Anderson); also of the bituminous shale of Dorsetshire, and of coal (Williams); and by distilling cinchonine with caustic potash. (Williams.)

*Preparation.* 1. *From Bone-oil.*—The oily mixture of volatile alkaloids obtained from bone-oil in the preparation of petinine (x, 150) and dehydrated by hydrate of potash, yields by fractional distillation: at 65°, propylamine, $C^6NH^9$; at 120° pyridine, $C^{10}NH^5$; between 132° and 137°, picoline, $C^{12}NH^7$; and between 152° and 155°, principally lutidine. This latter portion saturated with hydrochloric acid, deposits, after addition of bichloride of platinum, a pure salt of picoline, and afterwards a mixture of picoline and lutidine salts; the mother-liquor treated with alcohol and ether yields a pure salt of lutidine. (Anderson.)

¶. *From Shale naphtha and Coal-tar naphtha.*—The thick and treacly matter produced by agitating crude shale naphtha with oil of vitriol for the purpose of purification, was repeatedly boiled with water to resinise and separate the tar, during which process a large quantity of Runge's pyrrol was evolved, as shown by the purple colour which the vapour imparted to slips of wood moistened with hydrochloric acid. The liquid was then evaporated to a small bulk, saturated with lime or potash, distilled, and the product supersaturated with hydrochloric acid to separate the non-basic oil. The solution was distilled with an alkali to separate the oily bases, which were then freed from a small quantity of ammonia by washing with strong potash-ley, and dehydrated by means of sticks of potash. The anhydrous oily bases were then subjected to repeated fractional distillation, whereby they were divided into two groups, the first boiling below 160°, and being soluble in water, while the rest, which boiled at higher temperatures, were perfectly insoluble. After about six rectifications, the portion boiling below 160°, which was at first very small, amounted to more than all the rest united.—The portion of this latter distillate which passed over between 93° and 98°,

contained pyridine, picoline and lutidine, which were separated by the fractional crystallisation of their platinum-salts (x, 407); the portion boiling between 132° and 138° consisted of lutidine mixed with a small quantity of picoline; the portion which passed over between 150° and 153°, and likewise between 177° and 183°, consisted of pure lutidine; and that which distilled between 194° and 225°, was chiefly lutidine mixed with collidine ($C^{16}NH^{11}$). This latter base also passed over between 225° and 255°. Lastly the very small portion which distilled above 260° contained parvoline $C^{18}NH^{13}$.

By a similar process, lutidine may be obtained from coal-tar; the distillate obtained between 150° and 155° contains lutidine together with picoline. (Williams, *N. Ed. Phil. J.* [2], 2, 324; *Chem. Gaz.* 1855, 401.)

3. *From Cinchonine.* — Cinchonine was distilled with hydrate of potash in an iron retort, and the product, which always contained pyrrol, was collected in a well-cooled receiver, afterwards acidulated and boiled for two days to remove the pyrrol. The bases were then set free by the addition of caustic potash-solution, dehydrated by sticks of potash, and subjected to repeated fractional distillation, whereby fractions were obtained as low as 154° to 160° and as high as 271°. The more volatile portion consisted of lutidine together with small portions of picoline and pyridine, from which it was separated by nine rectifications, the portion boiling between 160° and 165° being collected apart. — The next portion of the distillate, between 179° and 182°, contained collidine, and the portion which boiled above 200° contained a set of bases belonging to a different series, viz., chinoline, $C^{18}NH^{7}$ and lepidine $C^{20}NH^{9}$. — The alkaline distillate obtained by heating cinchonine with potash was formerly regarded as a single base to which the name chinoline was applied. (Williams.) ¶.

*Properties.* More oily than picoline. Its odour is less pungent and more aromatic. (Anderson.) Boils at about 160°. Sp. gr. about 0·93. (Williams.)

| | | Anderson. *from bone-oil.* | Anderson. *from cinchonine.* | C. Greville Williams. *from shale-naphtha.* *a.* | *b.* | *c.* |
|---|---|---|---|---|---|---|
| 14 C | 84 | 78·51 | 78·45 | 78·68 | 78·68 | 78·65 | 78·75 |
| N | 14 | 13·08 | | | | | |
| 9 H | 9 | 8·41 | 8·41 | 8·52 | 8·85 | 88·6 | 8·92 |
| $C^{14}NH^{9}$ | 107 | 100·00 | | | | | |

Of the three specimens of lutidine from shale-naphtha analysed by Williams, *a* distilled over between 150° and 155°; *b* between 177° and 183° sp. gr. 0·928; and *c* between 194° and 225°; this last portion also contained collidine, which increases the percentage of carbon and hydrogen.

¶ *Decompositions.* 1. Vapour of lutidine passed over red-hot lime is converted, with deposition of carbon, into another base called by Williams *carmidine*, the composition of which has not yet been ascertained. It produces a fine red colour with firwood and hydrochloric acid, and bluish green with chloride of lime. (Williams.) ¶.

*Combinations.* Lutidine is sparingly soluble in cold water, and the dissolved portion immediately separates in the form of an oily layer.

The *salts of Lutidine* are very soluble.

*Chloromercurate of Lutidine.* — $C^{14}NH^{9},2HgCl$. — The alcoholic solutions of corrosive sublimate and hydrochlorate of lutidine yield a white granular precipitate, which dissolves in boiling water, with partial decomposition, and separates unaltered on cooling from solution in boiling alcohol. (Anderson.)

*Chloroplatinate of Lutidine.* — Four-sided tables often confused and irregularly formed. (Anderson.) Pale yellow ensiform crystals, nearly half an inch long, or ruby-coloured flat four-sided prisms. (Williams.) Dissolves readily in cold, and still more in hot water, and is likewise soluble in excess of hydrochloric acid. (Anderson.)

| | | Anderson. | C. Greville Williams. | | | | |
|---|---|---|---|---|---|---|---|
| | | | *a.* | *b.* | *c.* | *d.* | *e.* |
| 14 C | 84·0 | 26·81 | 26·35 | 26·94 | 26·14 | | |
| N | 14·0 | 4·49 | | | | | |
| 10 H | 10·0 | 3·19 | 3·23 | 3·36 | 3·16 | | |
| Pt | 98·7 | 31·51 | 31·40 | 31·14 | 31·76 | 31·66 | 31·[illegible] | 31·7 | 31·8 |
| 3 Cl | 106·5 | 34·00 | | | | | |
| $C^{14}NH^{10}Cl,PtCl^{2}$ | 313·2 | 100·00 | | | | | |

¶. Anderson's salt was prepared with lutidine, obtained from bone-oil; Williams's salt *a* with lutidine, obtained from cinchonine (B.P. 160°—165°); *b*, *c*, *d* and *e* with lutidine from shale-naphtha: *b* from the fraction of the distillate (p. 338), boiling between 132° and 138°; the mother-liquor of these crystals yielded the platinum-salt of picoline; *c* from the fraction distilling between 150° and 153° (the same as analysis *a*, page 338) *d* and *e* were obtained from the portion of the distillate which, in the first rectification, boiled below 98°, not by first separating the several bases contained in that portion by fractional distillation, and then converting them into platinum-salts, but by treating the whole of the liquid boiling below 98° with hydrochloric acid and chloride of platinum, and separating the several platinum-salts by fractional crystallisation (x. 407). The solution evaporated over oil of vitriol yielded: first the crystals *d* which were pale yellow, uniform and nearly half an inch long, together with thick flat four-sided ruby-coloured prisms; secondly the crystals *e*, which were thick prisms; thirdly, long, thin, square prisms of chloroplatinate of picoline containing 32·29 p. c. platinum (calc. 32·94); fourthly, short, hard, dark red prisms, also of picoline-salt containing 32·69 p. c. platinum; and fifthly, radiating needles of deep orange-yellow colour containing 34·71 p. c. platinum, which agrees nearly with the platinum-salt of pyridine (calc. 34·6 p. c.). This method of separating volatile oily bases by the crystallisation of the platinum-salts is recommended both by Anderson and by Greville Williams as greatly to be preferred to fractional distillation, because it entails much less waste; it has however the disadvantage of requiring a very large amount of platinum. To obtain correct results in the analysis of these platinum-salts, they should be pulverised, washed with a mixture of alcohol and ether to separate a peculiar resinous matter, and dried over oil of vitriol, as they decompose at 100°. ¶.

## *Conjugated Compounds containing* $C^{14}NH^{7}$ *or similar Nuclei.*

### ¶. Methyllutidine.

$$C^{16}NH^{11} = C^{14}AdH^{4}(C^{2}H^{3}),H^{2}.$$

C. Greville Williams. *Ed. Phil. Trans.* 21. Pt. ii, p. 317.

Lutidine mixed with twice its bulk of iodide of methyl becomes heated, boils, and almost immediately solidifies into a mass of crystals

consisting of hydriodate of methyllutidine. This salt (prepared with lutidine obtained by distilling cinchonine with potash) dissolves very easily in water and alcohol, but is nearly insoluble in ether. On evaporating its alcoholic solution to a syrup, it retains that state for some time, but as soon as it is touched, long beautiful needles shoot across the vessel, and the whole ultimately solidifies into a mass of crystals.

When this salt is treated with potash, no odour of a volatile base is evolved; hence methyllutidine appears to belong to Hofmann's fourth class of bases, formed on the ammonium type.

The *platinum-salt* $C^{14}NH^{12}Cl,PtCl^2$ was obtained by dissolving the hydriodate in water, precipitating the iodine with nitrate of silver, adding excess of hydrochloric acid, and mixing the filtrate with bichloride of platinum. It then yielded crystals containing 30·29 p. c. platinum (calculated quantity 39·16). ¶.

## Ethyltoluidine.

$C^{18}NH^{13} = C^{14}(C^4H^5)(NH^6),H^2$.

MORLEY & ABEL. *Chem. Soc. Qu. J.* 7, 68; *Pharm. Centr.* 1854, 507.

*Aethyltoluidine, Vinetoluidin.*

*Formation.* By the action of bromide or iodide of ethyl on toluidine. (Hofmann.)

*Preparation.* When toluidine is mixed with iodide of ethyl in a sealed tube and heated in the water-bath for two or three days, the whole becomes crystalline, and at length a layer of oil separates on the surface. The excess of iodide of ethyl is removed by distillation, and the residue, consisting of hydriodate of ethyltoluidine, is distilled with strong potash-ley; the base then passes over in the form of a light oil, which is removed and rectified over caustic potash.

*Properties* Colourless oil having an aromatic odour. Boils at 127°. Sp. gr. =0·939.

| | | | Morley & Abel. |
|---|---|---|---|
| 18 C | 108 | 80·00 | 79·90 |
| N | 14 | 10·37 | |
| 13 H | 13 | 9·63 | 9·78 |
| $C^{18}NH^{13}$ | 135 | 100·00 | |

Heated with iodide of ethyl, it yields biethyltoluidine.

*Hydriodate of Ethyltoluidine.* — *Preparation,* (vid. sup.) — Heavy oil having a peculiar alliaceous odour.

*Chloroplatinate of Ethyltoluidine.* — The solution of the hydrochlorate is evaporated, and carefully mixed with bichloride of platinum, and as soon as a precipitate appears, alcohol is added, which at first dissolves the precipitate, but deposits it again on agitation; the precipitate

washed with ether. Pale yellow, becoming dark-coloured at 100°; dissolves easily in water and alcohol. Contains 29·11 p. c. platinum and is therefore $C^{16}NH^{13},HCl,PtCl^2$. (Calculation requires 28·93 p. c. platinum.)

## Biethyltoluidine.

$$C^{22}NH^{17} = C^{14}(C^4H^5)^2NH^5,H^2.$$

MORLEY & ABEL. *Chem. Soc. Qu. J.* 7, 72.

When ethyltoluidine is heated in the water-bath with iodide of ethyl and the liquid gently agitated after two or three days, beautiful crystals form in it, which redissolve at the heat of the water-bath. The excess of iodide of ethyl is removed by distillation; the residue distilled with potash-ley; and the base which passes over in the form of a light oil, is rectified over caustic potash.

Colourless oil having the odour of ethyl-toluidine. Boils at 299. Sp. gr. = 0·924.

| | | | Morley & Abel. |
|---|---|---|---|
| 22 C | 132 | 80·98 | 80·90 |
| N | 14 | 8·59 | |
| 17 H | 17 | 10·43 | 10·47 |
| $C^{22}NH^{17}$ | 163 | 100·00 | |

*Hydriodate of Biethyltoluidine.*—Separates when its solution is evaporated over the water-bath, in oily drops which crystallise when touched with a glass rod. Decomposes in contact with the air, when heated over the water-bath, and by contact with alcohol. Contains 43·45 per cent. of iodine, and is therefore $C^{22}NH^{17},HI$. (Calculation, 43·66 p. c.)

## Triethyltoluidine.

$$C^{26}NH^{21} = C^{14}(C^4H^5)NH^4,H^2.$$

MORLEY & ABEL. *Chem. Soc. Qu. J.* 7, 73.

If it be supposed to contain 1 H more, it becomes *Triethyltoluylammonium* = $C^{14}H^5(C^4H^5)^3N$ (compare xi, 308).

Known only as a hydrate and in combination with acids.

Biethyltoluidine is heated with iodide of ethyl, till crystals form in the liquid. After the excess of iodide of ethyl has been distilled off, the hydriodate of triethyltoluidine remains in the form of a heavy oil, which, when heated with oxide of silver, forms an aqueous solution of *hydrate of triethyltoluidine*. This compound has a very bitter taste, a strong alkaline reaction, and precipitates the salts of baryta, strontia, lime, magnesia, alumina, chromic oxide and the heavy metallic oxides; the precipitates formed with the salts of alumina, lead-oxide, antimonic, stannous and

stannic oxide, are soluble in excess; the precipitate formed in cupric salts blackens on boiling. Mercuric salts are precipitated white.

*Chloroplatinate.* — Beautiful crystalline precipitate, insoluble in cold, but soluble in hot water, whence it crystallises in fine needles. Loses platinum when recrystallised.

| | | | Morley & Abel. |
|---|---|---|---|
| 26 C | 156·0 | 39·27 | 39·11 |
| N | 14·0 | 3·52 | |
| 22 H | 22·0 | 5·54 | 5·64 |
| Pt | 99·0 | 24·85 | 24·71 |
| 3 Cl | 106·2 | 26·82 | |
| $C^{26}NH^{22}Cl,PtCl^2$ | 397·2 | 100·00 | |

## Metoluidine.

$C^{30}N^3H^{17} = C^{28}CyNAdH^{13},H^2$.

WILSON. (1850.) *Chem. Soc. Qu. J.* 3, 15; *Ann. Pharm.* 77, 216; *Pharm. Centr.* 1851, 110.

*Formation.* In the decomposition of toluidine by chloride of cyanogen (p. 335).

*Preparation.* Toluidine is spread, by the application of a gentle heat, over a glass tube somewhat bent, and vapour of chloride of cyanogen is drawn over it by means of an aspirator; the heat evolved by the reaction is then sufficient to keep the substance in a state of fusion. The resulting resinous mass, consisting of hydrochlorate of metoluidine, is dissolved in water containing hydrochloric acid; the liquid filtered and precipitated by potash; and the precipitate is boiled for a while with the liquid containing potash, in order to drive off any undecomposed toluidine together with the watery-vapours, then washed with water, and recrystallised from alcohol.

Crystalline laminæ. The best crystals are obtained from a mixture of water and alcohol.

| | | | Wilson. |
|---|---|---|---|
| 30 C | 180 | 75·31 | 74·54 |
| 3 N | 42 | 17·58 | |
| 17 H | 17 | 7·11 | 7·34 |
| $C^{30}N^3H^{17}$ | 239 | 100·00 | |

Dissolves sparingly in cold, somewhat more readily in boiling water. Dissolves readily in hydrochloric acid.

*Chloroplatinate of Metoluidine.* — The hydrochloric acid solution of metoluidine forms with bichloride of platinum, a deep yellow precipitate which is insoluble in water and alcohol, and may be dried at 100°.

| | | | Wilson. |
|---|---|---|---|
| 30 C | 180 | 40·43 | 40·40 |
| 3 N | 42 | 9·43 | |
| 18 H | 18 | 4·04 | 4·24 |
| Pt | 99 | 22·17 | 22·15 |
| 3 Cl | 106·2 | 23·93 | |
| $C^{30}N^3H^{17},HCl + PtCl^2$ | 445·2 | 100·00 | |

## Cyanotoluidine.

$C^{32}N^4H^{18} = C^{28}Cy^2Ad^2H^{12},H^2.$

A. W. HOFMANN. (1848.) *Ann. Pharm.* 66, 144; *Chem. Soc. Qu. J.* 1, 159; *N. Ann. Chim. Phys.* 24, 67; *J. pr. Chem.* 51, 216; *Pharm. Centr.* 1848, 582.

*Formation* (p. 335).

*Preparation.* When chloride of cyanogen is passed through an alcoholic solution of toluidine, the red-brown liquid deposits after a few hours a crystalline mixture of several substances, from which hydrochloric acid extracts cyanotoluidine. This compound resembles cyaniline in every respect, excepting that it is less soluble in alcohol and ether.

## Thiotolamic Acid.

$C^{14}NH^9S^2O^6 = C^{14}AdH^7,2SO^3.$ ?

L. HILKENKAMP. (1855.) *Ann. Pharm.* 95, 96.

*Thiotoluolsäure.*

*Formation.* By the action of sulphite of ammonia on nitrotoluol. Known only in combination with bases.

*Preparation of the Ammonia-salt.* A mixture of 60 grm. nitrotoluol, 400 grm. of a cold-saturated aqueous solution of sulphite of ammonia, a small quantity of ammonia, and a litre of absolute alcohol, is placed in a flask provided with a condensing apparatus, and heated to the boiling point in the water-bath, the distillate being from time to time poured back into the flask, till a sample of the liquid is no longer clouded by water. The addition of carbonate of ammonia prevents the liquid from turning acid and the consequent decomposition of the thiotolamic acid produced. The cooled liquid is decanted from the crystallised sulphite of ammonia and evaporated, with addition of a small quantity of carbonate of ammonia; on cooling, it deposits radiating groups of delicate laminæ, which are filtered off and treated with ether, in which, after stirring, the adhering mother-liquor sinks, so that the laminæ may be poured off together with the ether; they are then quickly heated to between 50° and 60° and placed in vacuo. By a repetition of this process, they are obtained in a state of purity. From the mother-liquor, small nodules separate, which when recrystallised from alcohol, yield thiotolamate of ammonia in laminæ.

*Thiotolamate of Ammonia* forms delicate laminæ having a silky lustre and unctuous to the touch. It is very soluble in water, so that it cannot be crystallised therefrom; it also dissolves readily in alcohol, but is insoluble in ether. The aqueous solution has a faint yellow colour, a peculiar sweet odour, and a slight acid reaction.

| | | | Hilkenkamp. |
|---|---|---|---|
| 14 C | 84 | 41·18 | 40·84 |
| 2 N | 28 | 13·72 | 14·08 |
| 12 H | 12 | 5·89 | 6·35 |
| 2 S | 32 | 15·68 | 15·41 |
| 6 O | 48 | 23·53 | 23·32 |
| $C^{14}NH^5(NH^4),2SO^2$ | 204 | 100·00 | 100·00 |

This acid bears the same relation to toluol that thionaphthamic acid bears to naphthalin.

In damp air, the salt gradually acquires a rose-red tint. Heated on platinum foil, it melts and chars. Sulphuric, hydrochloric and nitric acids do not produce any alteration in the aqueous solution, even at the boiling heat. The acid solutions assume a rose-colour when exposed to the air. Nitrate of silver is decomposed by the aqueous solution of the salt after a while, and more quickly by the alcoholic solution with precipitation of metallic silver. Aqueous sesquichloride of iron acquires a purple-red colour when mixed with it, and after a while a black precipitate is deposited. The dilute solutions of sulphate and chloride of copper are coloured green by it, the former becoming turbid when heated. In a solution of corrosive sublimate, calomel is precipitated. A solution of protocyanide of iron is rendered turbid by it and gives off a faint odour of hydrocyanic acid; similarly with ferricyanide of potassium, only the turbidity does not show itself so quickly. By the action of chlorine, a heavy yellowish oil is produced smelling like chloranil.

*Thiotolamate of Potash.* — When thiotolamate of ammonia is added to aqueous carbonate of potash and heated as long as ammonia continues to escape, the liquid evaporated to dryness over the water-bath, the residue exhausted with boiling absolute alcohol, and the solution filtered hot, it deposits small nodules, which when dry form a powder having a faint reddish tint. This salt is less soluble in water and alcohol than the ammonia-salt.

| | | | Hilkenkamp. |
|---|---|---|---|
| $C^{14}NH^5S^2O^6$ | 186 | 82·59 | |
| K | 39·2 | 17·41 | 17·22 |
| $C^{14}NH^5KS^2O^6$ | 225·2 | 100·00 | |

*Thiotolamate of Soda.* — Prepared like the potash-salt. Small crystalline nodules which form a white powder when dry. Easily soluble in water, sparingly in alcohol, insoluble in ether.

*Thiotolamate of Baryta.* — The ammonia-salt is added to boiling water and the liquid kept at the boiling heat as long as ammonia continues to escape; the excess of baryta precipitated by carbonic acid, and

the filtered liquid evaporated, whereupon it deposits white crystalline crusts. The salt dissolves readily in hydrated alcohol, but is insoluble in absolute alcohol and in ether.

## Salhydramide. $C^{42}N^2H^{18}O^6$.

ETTLING. (1839.) *Ann. Pharm.* 29, 309; 35, 261; *Pharm. Centr.* 1840, 836.
LAURENT. *Rev. scient.* 16, 393.

*Salicylimide, Hydrure d'Azosalicyle.*

*Formation.* By the action of ammonia (or hydrosulphate of ammonia) on salicylous acid:

$$3C^{14}H^6O^4 + 2NH^3 = C^{42}N^2H^{18}O^6 + 6HO.$$

Corresponds to hydrobenzamide (p. 191).

*Preparation.* 1. When dry ammoniacal gas is passed over salicylous acid, a slight heat is evolved, the acid increases in weight and solidifies to a yellowish crystalline mass, which melts between 30° and 40° and yields a scanty sublimate. (Ettling.) 100 parts of dry salicylous acid take up, according to Ettling, 9·69 pts. of ammonia; according to the above equation, the quantity should be 9·29 pts.—2. One measure of salicylous acid is dissolved in 3 or 4 measures of alcohol, and 1 measure of aqueous ammonia is added. Yellowish white needles of salicylate of ammonia are then formed, which ultimately reduce the liquid to a nearly solid mass; but on applying a gentle heat, the whole dissolves, and the solution on cooling deposits heavy, deep yellow crystals of salhydramide (p. 338). If only a small quantity of alcohol is used, or if the liquid after it has become clear, is mixed with water, a brownish yellow oil separates which gradually changes into crystalline salhydramide. (Ettling.)

*Properties.* Deep yellow, shining, transparent, hard, four-sided prisms belonging to the double oblique prismatic system. *Fig.* 121 ($\infty$'P . $\infty$P' . oP). $u : v = 117° 30'$; $y : u = 93° 30'$; $y : v = 103° 30'$. (Laurent.) The alcoholic solution has an alkaline reaction.

| | | | | Ettling. |
|---|---|---|---|---|
| 42 C | 252 | | 72·83 | |
| 2 N | 28 | | 8·09 | 8·92 |
| 18 H | 18 | | 5·20 | 5·30 |
| 6 O | 48 | | 13·88 | |
| $C^{42}N^2H^{18}O^6$ | 346 | | 100·00 | |

*Decompositions.* 1. Melts at 300° into a brownish yellow mass and yields a very light white sublimate. The residue solidifies on cooling and forms a transparent mass, which chars when strongly heated.—2. It is not altered by dilute acids at ordinary temperatures, but when heated it is converted into salicylous acid and the ammonia salt of the acid employed.—3. When boiled with potash-ley, it gives off a large

quantity of ammonia and leaves salicylite of potash. The alcoholic solution may be mixed with weak potash without decomposing. — 4. When ammonia is poured upon it and left to evaporate in the air, the compound is gradually converted into a dingy yellow-green powder. The alcoholic solution mixed with ammonia quickly turns brown on exposure to the air and absorbs a volume of oxygen equal to its own. — 5. An alcoholic solution of salhydramide through which sulphuretted hydrogen is passed, yields thiosalicol.

*Combinations.* — Salhydramide appears to be insoluble in water.

*Lead-compound.* — *a.* When an aqueous solution of neutral acetate of lead is mixed with 10 times its bulk of alcohol, the mixture then heated, and, after addition of a little ammonia, mixed with a solution of salhydramide and a small quantity of ammonia, as long as the precipitate at first produced redissolves in the hot liquid, this liquid deposits on cooling, a deep yellow, heavy, granular powder, which, after being washed with water and dried, resembles chrome-yellow.

*b.* Neutral acetate of lead added to a solution of salhydramide mixed with ammonia and water, produces light yellow flakes, which when dry become strongly electrical by friction.

*Iron-compound.* — When ferric hydrochlorate is mixed with a sufficient quantity of tartaric acid to prevent precipitation by excess of ammonia and a solution of salhydramide in ammoniacal alcohol prepared hot, and containing so much ammonia that it is not rendered turbid by 40 times its volume of cold water, is added to it, the mixture immediately assumes a dark blood-red colour and deposits, after a few seconds, yellowish red flakes, which soon acquire a deeper and more fiery colour and a granular texture. The product is washed with water and dried. — If the iron solution is somewhat in excess, the precipitate quickly settles to the bottom. The mother-liquor is clear, and in the course of a few months deposits very small dark violet crystals which have a strong lustre and yield a red-brown powder. — Salicylous acid may also be used instead of salhydramide, but in that case the compound takes some time to separate.

Dark fiery-red, granular, like sesquioxide of iron Tolerably light.

| | | | Ettling. |
|---|---|---|---|
| $Fe^2O^3$ | 80 | 19·23 | 19·46 |
| 42 C | 252 | 60·57 | 60·57 |
| 3 N | 42 | 10·09 | 8·57 |
| 18 H | 18 | 4·33 | 4·30 |
| 3 O | 24 | 5·78 | 7·10 |
| $C^{42}N^3H^{18}O^3,Fe^2O^3$ | 416 | 100·00 | 100·00 |

According to Gerhardt, this compound is $C^{42}N^2fe^2(NfeH^2)H^{15}O^6$, that is to say, salhydramide in which 2 At. H are replaced by 2 At. fe, and 1 At. H by ferammonium (fe = $\frac{2}{3}$ Fe; ferammonium = $NfeH^3$, that is to say ammonium in which 1 At. H is replaced by fe).—The formation of the compound from free salicylous acid is explained in a manner similar to that of salhydramide, by the equation:

$$3C^{14}H^5O^3,Fe^2O^3,NH^3 + 2NH^3 = C^{42}N^3H^{18}O^3,Fe^2O^3 + 6HO \text{ [L.]}.$$

When heated above 100°, it melts, gives off white vapours, and leaves carburet of iron. — When boiled with water, it retains its fiery-red colour, but the amount of iron rises to 20·5 per cent. and the water

acquires a yellow colour, leaves a slight residue when evaporated, and forms with acetate of copper, a few spangles of the copper-compound of salhydramide. — It is not altered by cold very dilute nitric acid; but when heated with the stronger acid, it dissolves and forms a yellow solution which deposits salicylous acid on boiling. It is dissolved by hydrochloric acid diluted with alcohol, even in the cold; the solution mixed with bichloride of platinum, yields after a while a deposit of chloroplatinate of ammonium.—The solution in aqueous hydrochloric acid, forms with sulphuretted hydrogen, a precipitate of sulphur; with ferrocyanide of potassium, a precipitate of prussian blue after a while; with sesquicyanide of iron, it immediately acquires an emerald-green colour, and after a few hours deposits prussian blue.

It dissolves in alcohol, forming a dark blood-red solution, from which water throws down a lighter-coloured compound containing 29·5 p. c. ferric oxide; the supernatant liquid mixed with ammonio-cupric acetate does not form the copper-compound of salhydramide, but only a dingy greyish green precipitate.

*Copper-compound.* — When a very dilute solution of salhydramide is mixed with ammonio-cupric acetate, an emerald-green liquid is produced, which loses its colour in ten minutes and deposits emerald-green, shining, interlacing, crystalline laminæ; these are washed with alcohol, till that liquid runs through colourless, and then dried. If in the preparation of salicylite of copper (p. 243), the free acetic acid is neutralised with ammonia, this compound is precipitated together with oxide of copper.

Very light crystalline laminæ, of a dark-green colour and strong satiny lustre. From a solution in water mixed with a little ammonia and alcohol, it is precipitated of a pale blue-green colour on the addition of acetate of copper.

| | | | Ettling. |
|---|---|---|---|
| 3 Cu | 95·4 | 20·95 | 25·53 |
| 42 C | 252·0 | 55·34 | |
| 3 N | 42·0 | 9·22 | 8·97 |
| 18 H | 18·0 | 3·95 | 4·04 |
| 6 O | 48·0 | 10·54 | |
| $C^{42}N^3H^{18}Cu^3O^6$ | 455·4 | 100·00 | |

According to Gerhardt, it is salhydramide in which 2 At. H are replaced by 2 Cu, and 1 At. H by $NCuH^3$ (cuprammonium), so that its formula is $C^{42}N^2Cu^2(NH^3Cu)H^{15}O^6$. —The formation of the compound is represented by the equation:

$$2C^{14}CuH^5O^4 + C^{14}CuH^5O^4,NH^3 + 2NH^3 = C^{42}N^3Cu^3H^{18}O^6 + 6HO \text{ [L.]}.$$

When heated, it melts into a blood-red mass, and gives off a greenish vapour which condenses into oily drops, crystallising as they cool, perfectly volatile, and smelling like gum benzoïn. At a higher temperature, the residue solidifies and slowly burns, leaving oxide of copper. It dissolves in cold dilute hydrochloric acid, forming a green solution, and on neutralising the acid with potash, or even adding a rather large excess, the compound is precipitated in its original state. When heated with strong acids, it yields the ammonia-salt and the cupric salt of the acid, and gives off salicylous acid. It is not attacked by weak potash-solution in the cold, and but slowly attacked at the boiling heat. After boiling for some time, the liquid suddenly acquires a light copper colour, and deposits a red pitchy substance on the sides of the vessel, the rest of the liquid still retaining

a grass-green colour and containing spangles of the undecomposed substance. The aqueous or alcoholic solution is but slowly decomposed by sulphuretted hydrogen. The yellow filtrate smells of hydrosulphate of ammonia, and sulphide of copper remains on the filter.

The copper compound is nearly insoluble in water and in alcohol.

Salhydramide dissolves very sparingly in cold alcohol, in 50 pts. of hot alcohol, and crystallises out for the most part on cooling. Water does not precipitate the solution if it has been previously mixed with ammonia.

## Bromosalhydramide. $C^{42}N^{2}Br^{2}H^{15}O^{6}$.

PIRIA. (1838.) *Ann. Pharm.* 30, 175.

*Bromosamide.*

Produced by the action of ammonia on bromosalicylous acid; its reactions are exactly similar to those of chlorosalhydramide.

| | | | | | Piria. |
|---|---|---|---|---|---|
| 42 C | 252 | .... | 43·23 | ..... | 42·93 |
| 2 N | 28 | .... | 4·80 | ..... | 5·07 |
| 15 H | 15 | .... | 2·57 | ..... | 2·67 |
| 2 Br | 240 | .... | 41·17 | ..... | 40·70 |
| 6 O | 48 | .... | 8·23 | ..... | 8·63 |
| $C^{42}N^{2}Br^{2}H^{15}O^{6}$ | 583 | .... | 100·00 | ..... | 100·00 |

## Chlorosalhydramide. $C^{42}N^{2}Cl^{3}H^{15}O^{6}$.

PIRIA. (1835.) *Ann. Pharm.* 30, 172.

*Chlorosamide.*

*Formation.* By the action of ammoniacal gas on chlorosalicylous acid:

$$3C^{14}ClH^{5}O^{4} + 2NH^{3} = C^{42}N^{2}Cl^{3}H^{15}O^{6} + 6HO.$$

*Preparation.* Dry ammoniacal gas is passed over chlorosalicylous acid; the resulting resinous mass pulverised; ammoniacal gas again passed over it; and these operations repeated as long as any action takes place, that is to say, as long as water continues to form; the yellow mass is then dissolved in anhydrous alcohol or hot anhydrous ether, whence the chlorosalhydramide crystallises on cooling.

*Properties.* Yellow iridescent crystalline scales.

| | | | | | Piria. |
|---|---|---|---|---|---|
| 42 C | 252·0 | .... | 56·10 | ..... | 55·39 |
| 2 N | 28·0 | .... | 6·23 | ..... | 6·45 |
| 15 H | 15·0 | .... | 3·34 | ..... | 3·43 |
| 3 Cl | 106·2 | .... | 23·64 | ..... | 21·46 |
| 6 O | 48·0 | .... | 10·69 | ..... | 13·27 |
| $C^{42}N^{2}Cl^{3}H^{15}O^{6}$ | 449·2 | .... | 100·00 | ..... | 100·00 |

Heated with acids, it yields ammonia and chlorosalicylous acid. With hot hydrated alcohol it gives off ammonia.

It is insoluble in water, but colours that liquid yellow when left in contact with it for some time.

It dissolves in hot anhydrous *alcohol* and *ether*.

## ¶. Salicylosanilide.

$C^{26}NH^{11}O^2 = C^{14}(N.H,C^{12}H^5)H^5,O^2$.

L. SCHISCHKOFF. *Compt. rend.* 45, 272; *Ann. Pharm.* 104, 373.

When equal volumes of salicylous acid and aniline are heated together under the ordinary pressure, water separates, and the fluid mixture solidifies on cooling:

$$C^{14}H^6O^4 + C^{12}NH^7 - 2HO = C^{26}NH^{11}O^2.$$

Beautiful light yellow crystals which melt below 100°.

| | | | | Schischkoff. |
|---|---|---|---|---|
| 26 C | 156 | 79·10 | | 78·65 |
| N | 14 | 5·50 | | 7·06 |
| 11 H | 11 | 7·10 | | 6·00 |
| 2 O | 16 | 8·30 | | 8·29 |
| $C^{26}NH^{11}O^2$ | 197 | 100·00 | | 100·00 |

[= $N.(C^{12}H^5),(C^{14}H^5O^2),H$, aniline, in which 1 At. H is replaced by salicylosyl. Isomeric with benzanilide].

When heated with acids or alkalis, it yields aniline and salicylous acid. Its alcoholic solution is not decomposed by sulphuretted hydrogen.

Insoluble in water, easily soluble in *alcohol*. ¶.

### *Unknown Primary Nucleus* $C^{14}H^{10}$.

### *Oxygen-nucleus* $C^{14}H^8O^2$.

## Pyroguaiacin. $C^{14}H^8O^2$. ?

PELLETIER & DEVILLE. (1843.) *Compt. rend.* 17, 1143; *Pharm. Centr.* 1844, 95.

EBERMAIER. *J. pr. Chem.* 62, 291; *Pharm. Centr.* 1854, 289.

*Formation and Preparation.* Obtained together with guaiacene and pyroguaiacic acid in the dry distillation of guaiac resin; not perhaps from all varieties, inasmuch as it is not mentioned by Will (*Ann. Pharm.* 89, 345) among the products of distillation of that resin.

*Properties.* Nacreous laminæ, volatile without decomposition. (Pelletier & Deville.) When sublimed in a Mohr's apparatus, it forms laminæ or long needles. (Ebermaier.) Melts at 180°. (Pelletier & Deville.)

| | | | Pelletier & Deville. | Ebermaier. |
|---|---|---|---|---|
| 14 C | 84 | 77·78 | 76·95 | 78·46 |
| 8 H | 8 | 7·40 | 7·46 | 6·97 |
| 2 O | 16 | 14·82 | 15·59 | 14·57 |
| $C^{14}H^{8}O^{2}$ | 108 | 100·00 | 100·00 | 100·00 |

According to Ebermaier, it is $C^{14}H^{5}O^{2}$ (which requires 78·50 p. c. C and 6·54 H) and according to Knop (*Pharm. Centr.* 1844, 690) it is perhaps toluate of phenyl, $C^{28}H^{12}O^{4} = C^{12}H^{5}O,C^{16}H^{7}O^{3}$, which view however does not agree with the decomposition by sulphuric acid. This, as well as the reaction with chlorine, seems to imply that the substance examined by Ebermaier was not pure. [L.]

*Decompositions.* 1. With *nitric acid* it forms a purple-red solution. Similarly with aqueous chromic acid. — 2. When oil of vitriol is dropped into water in which pyroguaiacin is suspended and the liquid heated, the substance first turns yellow and then yields a rose-coloured solution, which afterwards turns green, and ultimately deposits a black-blue substance which colours the liquid violet. Oil of vitriol in contact with pyroguaiacin becomes very hot, and assumes first a brown, then a dingy green, and ultimately a dark blue colour, a black-blue substance then separating which contains sulphur, but not in the form of sulphuric acid. — 3. Pyroguaiacin suspended in water into which chlorine gas is passed, turns yellow, cakes together and then assumes a dark brown colour; the still moist product and the wash-water have a strong odour of musk which disappears on drying. — 4. Caustic ammonia colours pyroguaiacin yellow; the alcoholic solution saturated with ammonia yields nearly unaltered pyroguaiacin when evaporated. — 5. The alcoholic solution of pyroguaiacin reduces nitrate of silver.

Pyroguaiacin is insoluble in water.

Pyroguaiacin immersed in cold potash swells up considerably, and when the liquid is heated, forms a solution which solidifies on cooling into a solid mass, from which, after saturation with carbonic acid, alcohol extracts unaltered pyroguaiacin.

## Pyroguaiacic Acid.

$C^{14}H^{8}O^{4} = C^{14}H^{8}O^{2},O^{2}$. ?

UNVERDORBEN. (1826.) *Pogg.* 8, 402.
PELLETIER & DEVILLE. *Compt. rend.* 17, 1143.—*N. Ann. Chim. Phys.* 12, 228; *N. J. Pharm.* 6, 118; *J. pr. Chem.* 33, 318; *Pharm. Centr.* 1844, 45.
SOBRERO. *N. J. Pharm.* 4, 381; *Compt. rend.* 17, 677; *Pharm. Centr.* 1844, 19.
VÖLCKEL. *Ann. Pharm.* 89, 345; *Pharm. Centr.* 1854, 434.

*Pyrojaksäure, Guajakbrandsäure* (Unverdorben), *Pyroguajaksäure* (Völckel), *Hydrure de guajacile* (Pelletier & Deville), *Acide pyrogaique* (Sobrero).

*Preparation.* 1. The oil obtained by the dry distillation of guaiac resin is distilled with 6 pts. of water and ⅛ pt. hydrate of potash as long as the distillate exhibits any odour; the residual liquid is decanted

from the tar, diluted with 2 pts. of water, and exposed to the air, after which it is evaporated, with frequent renewal of the water, till it no longer smells. On subsequently distilling the liquid mixed with sulphuric acid, a yellowish green oil collects in the receiver below the water. (Unverdorben.)

2. The heavy oil which passes over in the distillation of guaiac resin is dissolved in potash; the solution diluted with water and boiled in the retort as long as any yellow light oil passes over; the residue mixed with a quantity of sulphuric acid not quite sufficient to convert the whole of the potash into sulphate; the separated oil dissolved in potash; the solution boiled in the retort till the milky water which has passed over becomes perfectly clear on the addition of a small quantity of potash; and the oil again separated (3 lbs. of resin thus treated yielded 160 grms. of oil). This oil is dried in vacuo over oil of vitriol (because chloride of calcium is somewhat soluble in it and gives off water in distillation) and rectified. It begins to boil slightly at 100°, and is in complete ebullition at 200°; only a small quantity however passes over from 200° to 203°, about ⅛ of the oil from 203° to 210°, half from 210° to 220°, and the small coloured residue between 220° and 230°. By repeated fractional distillation, it is freed from an admixed easily decomposible oil, and pure pyroguaiacic acid is ultimately obtained. (Völckel.)

3. When the mixture of guaiacene (x, 411,) and pyroguaiacic acid obtained by the dry distillation of guaiac resin is washed with water and carefully distilled, all the guaiacene passes over first, the pyroguaiacic acid distilling at a higher temperature only; the middle portion of the distillate obtained at about 210° contains the pure acid, which is obtained colourless by repeated rectification in an atmosphere of carbonic acid. — Another method is to decompose the lead-salt by sulphuric acid, shake up the liquid with ether, wash the ethereal solution with water, and rectify in a stream of carbonic acid. (Sobrero.) — The acid is very difficult to obtain pure; the purification is conducted like that of creosote. (Deville & Pelletier.)

*Properties.* Colourless oil; sp. gr. = 1·119 at 220° (Sobrero); 1·125 at 16° (Völckel). Has a faint peculiar odour resembling that of creosote, and a pungent peppery taste like that of cloves. Boils at 210° (Sobrero), at 205° (Völckel). Vapour-density = 4·49 (Deville & Pelletier); = 4·898 (Sobrero.) Does not redden litmus.

| | | | Sobrero. | Völckel. |
|---|---|---|---|---|
| 14 C | 84 | 67·74 | 68·78 | 68·92 |
| 8 H | 8 | 6·45 | 6·84 | 6·38 |
| 4 O | 32 | 25·81 | 24·38 | 24·70 |
| $C^{14}H^8O^4$ | 124 | 100·00 | 100·00 | 100·00 |

| | | |
|---|---|---|
| C-vapour | 14 | 5·8240 |
| H-gas | 8 | 0·5544 |
| O-gas | 2 | 2·2186 |
| Vapour of Pyroguaiacic acid | 2 | 8·5970 |
| | 1 | 4·2985 |

According to Sobrero, it is $C^{15}H^9O^4$; according to Völckel $C^{15}H^8O^4$.—The acid examined by Sobrero was not pure; in the pure state it is $C^{14}H^8O^4$ (Deville). The formula $C^{16}H^8O^4$ would require 70·5 per cent. of carbon. [L.]

*Decompositions.* 1. The acid burns with a white sooty flame. (Sobrero.) — 2. It is very violently attacked by nitric acid, even when very dilute and in the cold, with formation of oxalic acid and a red-brown resin. (Sobrero, Völckel.) In the state of aqueous solution, it is converted into a red-brown resin by liquids which readily give up oxygen, such as bichromate of potash, ferric sulphate, &c. (Völckel.) The alcoholic solution reduces gold and silver-salts to the metallic state, and ferric and cupric salts to ferrous and cuprous salts respectively. (Sobrero.)—3. With chlorine or bromine it forms a crystallisable acid, in which half the hydrogen is replaced by chlorine or bromine. (Pelletier & Deville.) With chlorine, it forms a crystallisable, easily fusible mass, which when gently heated sublimes in long white needles; iodine and bromine act in like manner. (Sobrero.) The crystalline substance disappears again when acted upon by a larger quantity of chlorine. (Völckel.) — 4. Exposed to the air in contact with aqueous potash, it gradually turns red and ultimately dark green. (Pelletier & Deville, Sobrero.) When pure, it does not exhibit this colouring, even after two months' exposure. (Völckel.)

*Combinations.* Pyroguaiacic acid is sparingly soluble in water.

It dissolves in oil of vitriol, and is precipitated by water in its original state. (Völckel.)

With bases it forms crystallisable salts which turn black in the moist state; it does not decompose carbonates. (Pelletier & Deville.) It dissolves readily in aqueous potash but does not decompose alkaline carbonates. (Pelletier & Deville.) It is insoluble in ammonia. (Sobrero.)

With potash and ammonia, it forms white crystallisable masses. (Völckel.)

The potash-salt assumes a blue colour when fused in contact with the air; it is but sparingly soluble in absolute alcohol, still less in ether. (Unverdorben.)

The salts of the alkaline earths and heavy metallic oxides are sparingly soluble in water. (Unverdorben.)

The alcoholic solution of the acid forms with basic acetate of lead, a precipitate which is insoluble in water, soluble in strong alcohol, and melts at 100°. (Sobrero.) The same compound is obtained when an alcoholic solution of the acid containing ammonia is mixed with an ammoniacal solution of acetate of lead. (Völckel.)

| | | | Sobrero. | Völckel. |
|---|---|---|---|---|
| 14 C | 84·0 | 24·16 | 25·55 | 25·62 |
| 8 H | 8·0 | 2·31 | 2·30 | 2·26 |
| 4 O | 32·0 | 9·18 | 9·45 | 9·31 |
| 2 PbO | 223·6 | 64·35 | 62·70 | 62·81 |
| $C^{14}H^{8}O^{4},2PbO$ | 347·6 | 100·00 | 100·00 | 100·00 |

Pyroguaiacic acid dissolves readily in *alcohol* and in *ether*.

## Orcin.

$C^{14}H^8O^4 = C^{14}H^8O^2,O^2$. ?

ROBIQUET. (1829.) *Ann. Chim. Phys.* 42, 236; *Br. Arch.* 36, 315. — *Ann. Chim. Phys.* 58, 320; *N. Br. Arch.* 5, 174.—*J. Pharm.* 21, 269; *J. pr. Chem.* 6, 130; *Ann. Pharm.* 15, 289; *Pharm. Centr.* 1835, 438; 1838, 690.
LIEBIG & WILL. *Ann. Pharm.* 27, 147.
DUMAS. *Ann. Pharm.* 27, 140; *J. pr. Chem.* 16, 422.—*Pharm. Centr.* 1838, 691.
SCHUNCK. *Ann. Pharm.* 41, 159; 54, 269; *Pharm. Centr.* 1845, 727.
GERHARDT. *Compt. chim.* 1845, 287.
STENHOUSE. *Phil. Trans.* 1848, 85; *Ann. Pharm.* 68, 93, 99; *J. pr. Chem.* 45, 180.—*Pharm. Centr.* 1848, 318.
STRECKER. *Ann. Pharm.* 68, 108.
LAURENT & GERHARDT. *N. Ann. Chim. Phys.* 24, 315; *N. J. Pharm.* 14, 304; *J. pr. Chem.* 45, 304.

*Sources.* Orcin appears to exist, partly ready formed, in the lichens used for the preparation of archil and litmus.

*Formation.* 1. By boiling orsellic acid with water and therefore also by boiling lecanoric (alpha-orsellic) acid, erythric acid, picroerythrin or evernic acid with alkalies, these latter substances being first converted into orsellic acid. — 2. By the dry distillation of lecanoric acid, erythric acid, evernic acid and picroerythrin.

*Preparation.* Dry *Variolaria dealbata* is exhausted by boiling alcohol; the solution freed by evaporation and cooling from the semiresinous body which separates; the remaining liquid evaporated to an extract; and this extract exhausted with water. The aqueous solution evaporated to a syrup deposits after a few days crystals of orcin, which may be purified by recrystallisation from water, with addition of animal charcoal, during which operation however the charcoal absorbs a considerable quantity of orcin. (Robiquet.) — 2. A roccella or a lecanora is macerated with milk of lime; the strained liquid boiled for a few hours in an open vessel, and evaporated to one-fourth; carbonic acid gas passed through it as long as a precipitate of carbonate of lime continues to form; and the filtrate evaporated to dryness over the water-bath. The residue is boiled with three or four times its bulk of strong alcohol; and the solution is filtered and set aside to crystallise; after three or four days, the dark coloured crystals are dried between paper and dissolved in three or four times their volume of anhydrous ether; and the filtered solution is left to evaporate in vacuo. The large six-sided crystals thus obtained become still paler by recrystallisation. (Stenhouse.)

3. Perfectly colourless orcin is obtained as follows: Orsellic or erythric acid is boiled with water for half an hour or an hour, whereupon a large quantity of carbonic acid is given off, and the evaporated solution (mixed perhaps with animal charcoal) deposits on cooling a large quantity of colourless crystals of orcin. — 4. Or, pure lecanoric acid, or its green mother-liquor (*vid.* preparation of lecanoric acid from *Lecanora parella*)

is boiled with strong baryta-water; the baryta precipitated after the decomposition is complete, by a stream of carbonic acid gas; and the liquid heated to the boiling point, filtered, concentrated, and left to evaporate. To purify the crystals, they are dissolved in hot water, and boiled with hydrate of alumina or ferric hydrate, till the liquid is nearly decolorised, and the solution is filtered and left to crystallise. The hydrate of alumina or ferric hydrate takes up the pigment with which the impure orcin is coloured; and on dissolving the alumina or oxide of iron in hydrochloric acid, the pigment remains in the form of a resinous mass insoluble in water, easily soluble in alcohol and ether. If the orcin still remains coloured, it is distilled from a retort, the distillation being interrupted as soon as the orcin vapours begin to carry colouring matter over with them. The aqueous solution of the distillate evaporated in vacuo or over oil of vitriol, yields nearly colourless crystals having only a slight yellowish or bluish red tint.

To obtain anhydrous orcin from the hydrated crystallised compound; the latter is dried in vacuo or over oil of vitriol, or repeatedly crystallised from anhydrous ether (Schunck), or, after drying at 100°, it is distilled in a small retort heated on all sides; a small quantity of water then passes over at first; but as soon as the mass arrives at a state of complete ebullition, a transparent colourless substance distils over, which after some hours becomes crystalline and opaque.

*Properties.* Colourless, crystalline. When freed from water by previous ebullition, it boils between 287 and 280°. (Dumas.) When quickly distilled it passes over unchanged. Vapour-density = 5·7. (Dumas.)

The aqueous solution has a very sweet but nauseating taste. It does not colour litmus.

| *Anhydrous.* | | | Robiquet. | Dumas. | Stenhouse. |
|---|---|---|---|---|---|
| 14 C | 84 | 67·74 | 66·81 | 67·58 | 68·04 |
| 8 H | 8 | 6·45 | 6·82 | 6·50 | 6·70 |
| 4 O | 32 | 25·81 | 26·37 | 25·92 | 25·26 |
| $C^{14}H^{8}O^{4}$ | 124 | 100·00 | 100·00 | 100·00 | 100·00 |

| | | |
|---|---|---|
| C-vapour | 14 | 5·8240 |
| H-gas | 8 | 0·5544 |
| O-gas | 2 | 2·2186 |
| Orcin-vapour | $\frac{3}{8}$ | 8·5970 |
| | 1 | 5·7314 |

Isomeric with saligenin.

*Decompositions.* 1. With nitric acid, orcin forms a solution which turns red when heated, then suddenly gives off large quantities of nitrous vapours; and deposits red resinous flakes, which are light red after drying, dissolve in alcohol with yellow, and in alkalis with brown colour, and are precipitated therefrom by acids. After boiling for some time, these resinous flakes redissolve, the liquid acquiring a deep yellow colour and being afterwards found to contain nothing but oxalic acid. — 2. Orcin boiled with bichromate of potash becomes dark brown after a while and yields a dark brown sediment; the decomposition is much accelerated by addition of sulphuric acid. — 3. When *bromine* comes in

contact with solid orcin or with the concentrated aqueous solution, hydrobromic acid is given off, with rise of temperature, and a brown crystalline mass is formed, consisting of terbromorcin coloured by a brown resin. (Dumas, Laurent & Gerhardt.) — In a current of *chlorine gas*, orcin melts with considerable rise of temperature and evolution of hydrochloric acid gas; the product solidifies into a crystalline mass of chlororcin. (Schunck, Stenhouse.) Orcin does not undergo any alteration when melted with iodine. (Schunck.)—4. Orcin moistened with a few drops of a solution of chloride of lime, first assumes a purple-red colour, like orsellic acid, but soon after becomes deep yellow. (Stenhouse.) — 5. By the simultaneous action of ammonia and oxygen in presence of water, orcin is converted into orcein:

$$C^{14}H^8O^4 + NH^3 + 6O = C^{14}NH^7O^6 + 4HO.$$

Dry orcin remains unaltered in dry air mixed with ammoniacal gas; but moistened orcin in a mixture of air and ammoniacal gas absorbs oxygen from the air and a large quantity of ammonia, forming orcein; with ammoniacal gas and pure oxygen, the absorption is more abundant, but instead of orcein a brown substance is produced. — If the air be excluded, the orcin is not coloured by ammonia. — The aqueous solution of orcin, mixed with a few drops of ammonia, gradually assumes a brownish yellow colour, and after two days' exposure to the air becomes dark brown-red. — Orcin placed under a bell-jar over aqueous ammonia, gradually assumes a darker brown colour; on the following day, it forms with water, a brown-red solution; but if it be exposed to the air for some time in the dry state, the brown colour changes to deep violet, and water forms with it a beautiful red-violet solution, especially on addition of a little more ammonia. (Robiquet.) — 6. The precipitate which aqueous orcin forms with ammonia and nitrate of silver, is reduced by boiling, with formation of a silver speculum, the liquid at the same time turning red. Terchloride of gold is reduced by aqueous orcin, slowly in the cold, immediately when heated, a dark brown powder separating at the same time. (Schunck.)

*Combinations.* With water. — *a. Hydrated Orcin.* — Anhydrous orcin rapidly absorbs moisture from the air and is converted into hydrated orcin. — Colourless needle-shaped crystals, consisting of oblique six-sided prisms generally with an oblique terminal face. $\infty P$. $\infty P\infty$.—$P\infty$ and sometimes oP. (Miller, *Ann. Pharm.* 68, 103); *Fig.* 103, without *m*-faces (Laurent & Gerhardt); $\infty P : \infty P = 101° 30'$ (Laurent), 102° 24′ (Miller); $\infty P\infty : oP = 83° 57'$ (Miller); $\infty P\infty : \infty P = 129° 15'$ (Laurent & Gerhardt); $\infty P\infty : -P\infty = 136° 30'$ (Laurent); 136° 16′ (Miller); the crystals cleave very easily in the direction of $\infty P\infty$. Hydrated orcin melts at a gentle heat, and boils at a stronger heat, all the water escaping at first and anhydrous orcin volatilising afterwards. It gives off 2 At. water in vacuo over oil of vitriol at 100° and when distilled.

| | *Crystallised.* | | | Dumas. | Will. | Schunck. | Stenhouse. |
|---|---|---|---|---|---|---|---|
| 14 C | 84 | 59·15 | 57·22 | 57·93 | 58·08 | 58·90 |
| 10 H | 10 | 7·04 | 6·87 | 6·75 | 7·24 | 6·82 |
| 6 O | 48 | 33·81 | 35·91 | 35·32 | 34·68 | 34·28 |
| $C^{14}H^8O^4 + 2Aq$ | 142 | 100·00 | 100·00 | 100·00 | 100·00 | 100·00 |

*b. Aqueous Orcin.* — Orcin dissolves very easily in water.

Aqueous orcin forms with ferric hydrochlorate a dark red precipitate, from which ammonia extracts orcin. (Schunck.)

*Lead-compound.* — *a.* Aqueous orcin is precipitated by basic acetate of lead, and the precipitate is boiled with the neutral acetate, and washed with water. (Dumas, Schunck.) The precipitate, which is white at first, even when the orcin has been added in excess, soon turns red in contact with the air. (Schunck.) — Orcin combines with *stearic acid*, forming a compound which is decomposed by alkalis, with separation of stearic acid and a substance which is coloured by ammoniacal vapours and dissolves in water and in ether, but appears to be different from orcin. (Berthelot, *Compt. rend.* 41. 452.) — *b.* An aqueous solution of orcin containing ammonia is mixed by drops with nitrate of lead till about half of it is precipitated, the precipitate then digested in the liquid, and washed with boiling water. (Dumas.)

| | | | Dumas. *a.* | Dumas. *b.* | Schunck. | Stenhouse. | |
|---|---|---|---|---|---|---|---|
| 4 PbO | 448 | 80·86 | 79·95 | 79·60 | 79·81 | 78·07 | 80·51 |
| 14 C | 84 | 15·16 | 15·75 | 15·34 | 13·91 | | |
| 6 H | 6 | 1·08 | 1·14 | 1·18 | 1·18 | | |
| 2 O | 16 | 2·90 | 3·16 | 3·88 | 5·10 | | |
| $C^{14}H^{6}Pb^{2}O^{4},2PbO$ | 554 | 100·00 | 100·00 | 100·00 | 100·00 | | |

With excess of neutral acetate of lead, aqueous orcin forms a precipitate which quickly turns red, and contains 82·83 p. c. lead. (Stenhouse).

Aqueous orcin does not precipitate sulphate of copper, corrosive sublimate, or nitrate of silver; on addition of ammonia, a flocculent precipitate is formed in the cold with nitrate of silver.

Orcin dissolves in *alcohol* and in *ether*.

It is absorbed, like colouring matters, by animal charcoal.

## Terbromorcin.

STENHOUSE. (1848.) *Phil. Trans.* 1848, 87; *Ann. Pharm.* 88, 96; *Pharm. Centr.* 1848, 318.

LAURENT & GERHARDT. *N. Ann. Chim. Phys.* 24, 317; abstr. *Compt. rend.* 27, 164; *N. J. Pharm.* 14, 304; *J. pr. Chem.* 45, 304; *Pharm. Centr.* 1848, 717.

***Bromorcid.***

*Formation and Preparation.* Bromine in contact with orcin, gives off a large quantity of hydrobromic acid, even at ordinary temperatures; the mass, which is liquid at first, but solidifies after the excess of bromine has been expelled, is dissolved in alcohol, water added during the boiling, and the supernatant liquid decanted from the impure crystals which first separate as the liquid cools. This liquid solidifies on cooling, in the form of yellowish needles having a silky lustre. (Laurent & Gerhardt.) — Bromine is added to a concentrated aqueous solution of orcin as long as any action takes place, and the precipitated brown-red crystalline mass is

separated from the liquid, washed with cold water, and purified from an admixture of brown odoriferous resin by digestion with weak alcohol and a small quantity of animal charcoal. (Stenhouse.)

*Properties.* Long white coherent needles. Inodorous, tasteless. Melts very easily, even in hot water, into an oil which crystallises on cooling.

| | | | | Stenhouse. | Laurent & Gerhardt. |
|---|---|---|---|---|---|
| 14 C | 84 | 23·27 | | 23·62 | 23·1 |
| 5 H | 5 | 1·39 | | 1·57 | 1·7 |
| 3 Br | 240 | 66·47 | | 68·00 | 66·0 |
| 4 O | 32 | 8·87 | | | 9·2 |
| $C^{14}Br^{3}H\ O^{4}$ | 361 | 100·00 | | | 100·0 |

*Decompositions.* 1. When heated, it gives off hydrobromic acid and an oil which crystallises on cooling and leaves a large quantity of charcoal. (Laurent & Gerhardt.) — 2. With potash-ley, it assumes a dark violet-brown colour, and forms with a large quantity of water a brown-red solution which is decolorised by acids. Ammonia does not produce this colour. (Laurent & Gerhardt.) — With alkalis it forms a brown solution, in which hydrochloric acid produces a yellow resinous precipitate. (Stenhouse.)

It is insoluble in *water*, but dissolves very easily in *alcohol* and *ether*.

## Chlororcin. $C^{14}Cl^{3}H^{5}O^{4}$.

STENHOUSE. *Phil. Trans.* 1848, 88; *Pharm. Centr.* 1848, 318.
E. SCHUNCK. *Ann. Pharm.* 54, 271.

*Chlororceid.*

*Formation and Preparation.* Dry chlorine gas is passed over orcin till the mass which is fused at first, cools and crystallises, after which the product is crystallised from hot water and alcohol. (Schunck.) When dry orcin or its aqueous or alcoholic solution is treated with chlorine gas, only a small quantity of crystalline chlororcin is obtained, but a large quantity of closely adhering dark brown resin which is difficult to separate. (Stenhouse.)

*Properties.* Chlororcin crystallises from its aqueous or alcoholic solution in white needles. Melts at about 58·9°, and becomes crystalline again on cooling. Heated in a glass tube, it volatilises partly undecomposed, leaving a brown residue; the vapour condenses into an oil which soon crystallises. — Tastes sharp and cooling after continued mastication. The solution reddens litmus strongly. (Schunck.)

*Decompositions.* 1. Heated on platinum foil, it volatilises, emitting an irritating, suffocating vapour, which burns slowly with a red, smoky, green-edged flame, and leaves a considerable residue. It is slowly

attacked by nitric acid; by continued boiling with that acid, a solution is formed containing free chlorine. — The aqueous solution is not precipitated by nitrate of silver; but a large quantity of chloride of silver is formed on boiling. Chloride of gold is instantly reduced. (Schunck.)

Chlororcin dissolves in boiling water; in a quantity of water not sufficient to dissolve it, it melts into a brown oil.

It dissolves in alkalis and is precipitated therefrom in its original state by acids, even after long boiling. It forms an insoluble compound with baryta. (Schunck.)

It dissolves in *alcohol.*

## Orcein.

$C^{14}NH^{7}O^{6} = C^{14}AdH^{5}O^{2},O^{4}$. ?

ROBIQUET. (1829.) *Ann. Chim. Phys.* 42, 245; *Br. Arch.* 16, 315.— *Ann. Chim. Phys.* 58, 320; *J. Pharm.* 21, 269; *J. pr. Chem.* 6, 130; *N. Br. Arch.* 5, 174; abstr. *Ann. Pharm.* 15, 289; *Pharm. Centr.* 1835, 438.—*J. Pharm.* 21, 387.

HEEREN. *Schw.* 59, 336.

DUMAS. *Ann. Pharm.* 27, 145; *J. pr. Chem.* 16, 422; *Pharm. Centr.* 1838, 691.

KANE. *Phil. Trans.* 1840, 285; *N. Ann. Chim. Phys.* 2, 21 and 147; *Ann. Pharm.* 39, 38; *Pharm. Centr.* 1839, 862; 1841, 565.

LAURENT & GERHARDT. *N. Ann. Chim. Phys.* 24, 315.

***Beta-orcein, Lichen-red, Flechtenroth*** (Heeren).

*Formation.* From orcin by the action of ammonia and oxygen (p. 355). It is therefore contained in archil.

*Preparation.* 1. *From Orcin.* — The brown mass (p. 355) formed from orcin by exposure for 24 hours to air containing ammonia, is gently heated, at last to 100°, in order to expel the whole of the ammonia, then dissolved in water; the solution is mixed with acetic acid, and the brown precipitate washed with cold water. (Robiquet.) Heeren, by digesting erythric acid for several days with a small quantity of ammonia at 40°, and agitating frequently, obtained lichen-red, which does not differ essentially from orcein.

2. *Preparation of Orcein, Erythroleic acid* and *Azerythrin from Commercial Archil,* according to Kane. — Commercial archil is slightly acidulated with hydrochloric acid, the solution evaporated to complete dryness, and the residue exhausted with alcohol, till that liquid is but slightly coloured by it. The alcoholic solution is then evaporated to dryness over the water-bath; and the dark brown-red residue is washed with water till the ammoniacal salt is completely extracted, then dried, pulverised and treated with ether, as long as it imparts any perceptible colour to that liquid. The powder, after being kept at 100° for two hours to expel the ether, has a fine amber-red colour and consists of orcein and alphorcein. (Kane, p. 368).

When the amber-red ethereal infusion of the alcoholic extract of commercial archil is evaporated to dryness over the water-bath, there

remains a semifluid oil, which becomes perfectly liquid when heated, makes grease-spots on paper, and after a few days still deposits a small quantity of orcein. To separate that substance completely, the oil is dissolved in the smallest possible quantity of ether; the liquid decanted from the undissolved orcein-powder; and evaporated at a very gentle heat; and the residue kept for some time at 100°, to expel the ether completely. — The *erythroleic acid* thus obtained is semifluid at ordinary temperatures and of a purple-red colour.

| | *Erythroleic acid.* | Kane. |
|---|---|---|
| 26 C | 64·84 | 64·70 |
| 22 H | 9·00 | 9 33 |
| 8 O | 26·16 | 25·97 |
| $C^{26}H^{22}O^{8}$ | 100·00 | 100·00 |

Exposed to the air for a few weeks, it gradually solidifies and is then no longer soluble in ether.

It is nearly insoluble in water, which is however coloured by it.

It dissolves in alkalis, and forms purple precipitates with metallic oxides. The lead-compound has a purple-crimson colour.

| | *At* 120°. | Kane. |
|---|---|---|
| PbO | 31·33 | 31·64 |
| 26 C | 44·36 | 43·41 |
| 22 H | 6·18 | 6·24 |
| 8 O | 18·13 | 18·71 |
| $C^{26}H^{22}O^{8}$,PbO | 100·00 | 100·00 |

Sometimes the analyses yield less oxygen.

Erythroleic acid is soluble in alcohol and ether, not in oil of turpentine (Kane, *Phil. Trans.* 1840, 295; *N. Ann. Chim. Phys.* 2, 34; *Ann. Pharm.* 39, 47.

When the portion of archil which is insoluble in alcohol is repeatedly boiled with water, the first water acquires a rose-red colour, the second, a yellow. When the dark-red residue insoluble in water is boiled with potash-ley, woody fibre remains undissolved; and on mixing the potash-solution with an acid, evaporating to dryness, and exhausting the potash-salt with water, a small quantity of *azerythrin* remains behind; it is difficult however to obtain this substance free from azolitmin.

Dark red powder.

| | *Azerythrin.* | Kane. |
|---|---|---|
| 22 C | 39·69 | 38·80 |
| N | 4·11 | |
| 19 H | 5·38 | 5·70 |
| 22 O | 51·29 | |
| $C^{22}NH^{19}O^{22}$ | 100·00 | |

Azerythrin yields by combustion, 1 vol. nitrogen to between 20 and 21·8 oxygen.

When heated, it yields water and empyreumatic products, without fusing.

It is insoluble in water.

It dissolves in alkalis with wine-red colour (if it contains azolitmin, the solution has a violet or blue colour). It is not precipitated by acids. The solution forms brown-red precipitates with the salts of the heavy metals.

*Lead-compound of Azerythrin.* — The potash-solution is neutralised with acetic acid, precipitated by basic acetate of lead, and the precipitate dried at 82°.

| | | | Kane. |
|---|---|---|---|
| 3 PbO | 49·60 | | 49·79 |
| 22 C | 19·51 | | 19·33 |
| N | 2·07 | | |
| 19 H | 2·81 | | 3·00 |
| 22 O | 26.01 | | |
| $C^{22}NH^{19}O^{23},3PbO$ | 100·00 | | |

The compound does not dissolve in alcohol or ether.

*Properties of Orecin.* — Brown amorphous powder.

| I. | | | | II. | | | | Dumas. | Kane. |
|---|---|---|---|---|---|---|---|---|---|
| 18 C | 108 | 55·12 | | 14 C | 84 | 54·91 | | 55·1 | 54·19 |
| N | 14 | 7·13 | | N | 14 | 9·13 | | 7·9 | |
| 10 H | 10 | 5·10 | | 7 H | 7 | 4·57 | | 5·2 | 5·11 |
| 8 O | 64 | 32·65 | | 6 O | 48 | 31·39 | | 31·8 | |
| $C^{18}NH^{10}O^{8}$ | 196 | 100·00 | | $C^{14}NH^{7}O^{6}$ | 153 | 100·00 | | 100·0 | |

According to Calculation II, the formation of orcein from orcin is explained by the equation: $C^{14}H^{8}O^{4} + NH^{3} + 6O^{2} = C^{14}NH^{7}O^{6} + 4HO$ (Gerhardt). According to Kane, the formula II agrees best with the analyses of orcein and of its compounds, but does not explain the relation of orcein to orcin. Dumas gives the formula $C^{16}NH^{9}O^{7}$, which does not agree so well with the analyses.

*Decompositions.* 1. Orcein subjected to dry distillation yiel s ammoniacal vapours. — 2. Boiled with *potash-ley*, it gives off ammonia; the solution, even after continued boiling, yields with acetic acid, a considerable quantity of unaltered orcein, which however becomes resinous when dry and exhibits a conchoidal fracture. — 3. Orcein suspended in water and dissolved in alcohol, is converted by the action of *chlorine* into brown chlororcein, while only traces of hydrochloric acid are produced. (Kane.) — 4. Orcein is decolorised by sulphuretted hydrogen. When the lead-compound of orcein is decomposed by sulphuretted hydrogen, the precipitate does not impart any colour to boiling alcohol, but after addition of ammonia it immediately acquires a violet colour. (Kane.) An ammoniacal solution of orcein acidulated with hydrochloric acid is decolorised by zinc, but becomes red again when exposed to the air; ammonia throws down a white precipitate of the compound of leucorcein with oxide of zinc, which on exposure to the air acquires a violet and ultimately a purple colour. (Kane.)

*Combinations.* Orcein dissolves sparingly in water, but colours it, an is precipitated from the solution by metallic salts.

2. It dissolves readily in potash or ammonia, forming a solution of a splendid purple-red colour from which the colouring matter is precipitated by excess of common salt. — 100 pts. of dry orcein absorb, with evolution of heat, 8·06 pts. of ammoniacal gas (= 1 At. according to Kane); the compound has a deep violet colour and gives off all its ammonia at 100°.

*Preparation of Orseille* or *Archil.*—There are two varieties, viz., *orseille de mer*, which is obtained from various lichens of the genus *Roccella* growing on the rocky coasts of the Azores, the Canary and Cape de Verd isles, also of the Cape of Good Hope, Madeira, Corsica, Sardinia, &c., — and *orseille de terre*, for the preparation of which, *Variolaria orcina* (Ach.) from Auvergne, *Variolaria dealbata* (D. C.) from the Pyrenees, *Lecanora tartarea* and others from Sweden are employed. The largest amount of colouring matter is obtained from *Roccella Montagnei* from Angola, viz., 12 per cent.; *Lecanora tartarea* contains only from 1½ to 2 per cent. The cleansed and crushed lichens are rubbed up to a thin paste with water and putrefied urine or carbonate of ammonia, and left to ferment, with addition of quick lime, a small quantity of alum or arsenious acid being sometimes added perhaps to check putrefaction. In a week a violet colour is obtained, which becomes brighter in a fortnight; sometimes also an odour of violets is evolved. Orseille is kept in the moist state. — The colouring matter of orseille consists mainly of orcein; its decoction is dark-red, but becomes lighter when treated with acids, and violet with alkalis.

*Persio, Cudbear, Archil* is prepared in England from Swedish *Lecanora tartarea*, or from the rock-lichens of Wales or the Orkneys, in the same manner as French orseille. It is sent into the market in the form of a purple or violet powder.

3. The alkaline solution of orcein forms with metallic salts purple-red lakes of several shades, which lose much of their beauty in drying.

*Zinc-compound of Orcein.* — Violet.

| I. | | | | II. | | | | Kane. |
|---|---|---|---|---|---|---|---|---|
| 3 ZnO | 121·5 | 34·37 | | 2 ZnO | 81 | 31·11 | | 33·71 |
| 18 C | 108·0 | 30·55 | | 14 C | 84 | 32·18 | | 30·86 |
| N | 14 0 | 3·96 | | N | 14 | 5·36 | | |
| 14 H | 14·0 | 3·96 | | 10 H | 10 | 3·83 | | 4·10 |
| 12 O | 96·0 | 27·16 | | 9 O | 72 | 27·52 | | |
| $C^{18}NH^{10}O^{8},3ZnO+4Aq$ | 353·5 | 100·00 | | $C^{14}NH^{7}O^{6},2ZnO+2Aq$ | 261 | 100·00 | | |

*Lead-compound.* — The solution of orcein in ammonia is neutralised with acetic acid and precipitated with neutral acetate of lead. Purple precipitate which gives off 13·94 p. c. water at 100°, but is not completely dehydrated even at 121°. (Kane.)

| I. | | | II. | *At* 121°. | | Kane. |
|---|---|---|---|---|---|---|
| 3 PbO | 835·4 | 61·05 | 5 PbO | 559 | 62·05 | 62·76 |
| 18 C | 108·0 | 19·66 | 28 C | 168 | 18·64 | 18·66 |
| N | 14·0 | 2·55 | 2 N | 28 | 3·11 | |
| 12 H | 12·0 | 2·18 | 18 H | 18 | 2·00 | 2·27 |
| 10 O | 80·0 | 14·56 | 16 O | 128 | 14·20 | |
| $C^{18}NH^{10}O^{8},3PbO+2Aq$ | 549·4 | 100·00 | $2C^{14}NH^{7}O^{6},5PbO+4Aq$ | 901 | 100·00 | |

*Copper-compound.* — Prepared like the lead-compound. Has a dark purple colour. Gives off 10·6 per cent. of water at 100°, but is not completely dehydrated. (Kane.)

| I. | | | II. | | | Kane at 100°. |
|---|---|---|---|---|---|---|
| 3 CuO | 118·4 | 33·86 | 2 CuO | 79·6 | 30·62 | 32·37 |
| 18 C | 108·0 | 30·78 | 14 C | 84·0 | 32·34 | 30·26 |
| 14 H | 14·0 | 3·99 | 10 H | 10·0 | 3·95 | 3·92 |
| N | 14·0 | 3·99 | N | 14·0 | 5·40 | |
| 12 O | 96·0 | 27·38 | 9 O | 72·0 | 27·69 | |
| $C^{18}NH^{10}O^{8},3CuO+4Aq$ | 350·4 | 100·00 | $C^{14}NH^{7}O^{6},2CuO+3Aq$ | 259·6 | 100·00 | |

*Silver-compound.* — Obtained by boiling orcein with water, adding a few drops of ammonia, boiling for a while to expel the excess of ammonia, and mixing the liquid, which has a splendid violet colour, with nitrate of silver. Dark violet precipitate, becoming nearly black when pressed. (Dumas.)

| I. | | | II. | | | Dumas. |
|---|---|---|---|---|---|---|
| 2 AgO | 232 | 56·59 | 2 AgO | 232 | 63·31 | 58·6 |
| 18 C | 108 | 26·34 | 14 C | 84 | 22·90 | 24·6 |
| N | 14 | 3·41 | N | 14 | 3·81 | 3·5 |
| 8 H | 8 | 1·95 | 5 H | 5 | 1·36 | 1·8 |
| 6 O | 48 | 11·71 | 4 O | 32 | 8·62 | 11·5 |
| $C^{18}NAg^{2}H^{8}O^{6}$ | 410 | 100·00 | $C^{14}NAg^{2}H^{5}O^{6}$ | 367 | 100·00 | 100·0 |

Orcein dissolves with scarlet colour in *alcohol* and is precipitated therefrom by water; it is nearly insoluble in *ether*. (Kane.)

## Chlororcein.

KANE. *N. Ann. Chim. Phys.* 2, 152; *Pharm. Centr.* 1841, 573.

Chlorine gas is passed into water containing orcein or into an ammoniacal solution of orcein, whereupon the orcein gradually assumes a brownish yellow colour; the passage of the gas must be stopped as soon as the decomposition is complete, because an excess of chlorine would produce an alteration in the chlororcein. This substance is insoluble in water, but dissolves, with brownish yellow colour in alcohol, ether and ammonia; the ammoniacal solution is precipitated by acids and by metallic salts.

| | | | Kane. |
|---|---|---|---|
| 18 C | 108·0 | 40·48 | 39·63 |
| N | 14·0 | 5·25 | |
| 10 H | 10·0 | 3·75 | 4·34 |
| 2 Cl | 70·8 | 26·53 | 26·50 |
| 8 O | 64·0 | 23·99 | |
| $C^{18}NClH^{8}O^{4},HCl$ | 266·8 | 100·00 | |

Kane's analysis cannot be made to agree with the second formula for orcein; Gerhardt suggests that the substance analysed may have been impure.

Chlororcein dissolves in aqueous ammonia and potash. The solution contains sal-ammoniac and chloride of potassium. Acids added to this solution, precipitate chlororcein more or less decomposed.

## Leucorcein. $C^{18}NH^{19}O^{8}$. ?

KANE. *N. Ann. Chim. Phys.* 2, 147; *Pharm. Centr.* 1841, 522.

Known only in combination with oxide of zinc. — The zinc-oxide is added to an ammoniacal solution of orcein slightly acidulated with hydrochloric acid; the decolorised liquid precipitated by ammonia; and the white precipitate is collected on a filter in an atmosphere of carbonic acid, washed with boiling water, and dried in vacuo over oil of vitriol. During these operations, in spite of every precaution, the precipitate acquires a pale violet colour arising from incipient oxidation. — After drying over oil of vitriol in vacuo, it is $C^{18}NH^{12}O^{8},3ZnO + 2Aq$ and gives off 2 At. water when heated to 140° in a stream of carbonic acid.

| | *In vacuo.* | | | Kane. |
|---|---|---|---|---|
| 3 ZnO | 121·5 | .... | 36·00 | 35·22 |
| 18 C | 108·0 | .... | 32·00 | 31·31 |
| N | 14·0 | .... | 4·15 | 4·65 |
| 14 H | 14·0 | .... | 4·15 | |
| 10 O | 80·0 | .... | 23·70 | |
| $C^{18}NH^{12}O^{8},3ZnO + 2Aq$ | 337·5 | .... | 100·00 | |

| II. | *At* 140°. | | | Kane. |
|---|---|---|---|---|
| 3 ZnO | 121·5 | .... | 38·03 | 37·33 |
| 18 C | 108·0 | .... | 33·80 | |
| N | 14·0 | .... | 4·38 | |
| 12 H | 12·0 | .... | 3·76 | |
| 8 O | 64·0 | .... | 20·03 | |
| $C^{18}NH^{12}O^{8},2ZnO$ | 319·5 | .... | 100·00 | |

The compound absorbs oxygen very quickly from the air, and is converted into the violet compound of orcein and zinc-oxide.

## Azolitmin.

KANE. *N. Ann. Chim. Phys.* 2, 129, 137; *Ann. Pharm.* 39, 57; *Pharm. Centr.* 1841, 569.

*Preparation of Azolitmin and of the other colouring matters contained in Litmus.* (Kane, *Phil. Trans.* 1840, 298; *N. Ann. Chim. Phys.* 2, 129; compare Gélis, *J. Pharm.* 27, 477.) *a.* Commercial litmus in the state of powder is boiled with water as long as the water acquires any colour from it. The decoction, which contains but little colouring matter in proportion to the depth of its tint, is precipitated by neutral acetate of lead; the purple precipitate is decomposed by sulphuretted

hydrogen; the resulting mixture is washed with pure water, and afterwards with water containing ammonia; the dark brown liquid filtered from the sulphide of lead is evaporated to dryness; and the residue is moistened with hydrochloric acid and washed with hot alcohol to extract the sal-ammoniac. The residue then consists of pure *Azolitmin*: sometimes however this substance is mixed with *Spaniolitmin*; or this latter body may even constitute the entire residue.

*b.* The pale blue powder which remains after litmus has been thoroughly boiled with water, is made up into a thin paste with water, and hydrochloric acid is added till effervescence ceases and the liquid exhibits a strong alkaline reaction. The mass is then thrown on a filter; and the residue, after being freed from excess of acid by washing with water, is well dried and repeatedly boiled with alcohol, as long as that liquid extracts anything from it. The alcoholic solution is evaporated to dryness over the water-bath, and the residue digested with warm ether as long as the ether is coloured by it. The ethereal solution, distilled in the water-bath to remove the ether, leaves *Erythrolein* in the form of a purple semifluid oil. The portion of the alcoholic extract which is insoluble in ether consists of *Erythrolitmin*.

*c.* 1. The red-brown powder which remains after the boiling with alcohol (*vid. sup.*) consists of impure *Azolitmin*. This substance is either boiled with pure water, and pure azolitmin obtained by evaporating the strongly coloured solution; — or the residue insoluble in alcohol is boiled with ammoniacal water, and the blue solution evaporated to dryness, during which operation the greater part of the ammonia escapes; the remainder is separated by moistening the mass with hydrochloric acid, and washing the resulting sal-ammoniac with alcohol. — 2. The strongly coloured liquid obtained by boiling litmus with water is precipitated with neutral acetate of lead; the precipitate is washed with water, treated while still moist with sulphuretted hydrogen, and suspended in warm ammoniacal water; the dark blue liquid is evaporated to dryness, and moistened with hydrochloric acid; and the sal-ammoniac is separated by means of warm alcohol. — The residue is but of small amount in proportion to the deep colour of the solution; it sometimes consists of pure azolitmin, more rarely of spaniolitmin, a substance not containing nitrogen.

*Properties of Azolitmin.* Dark brown-red amorphous powder.

| I. | | | | II. | | | | Kane at 100°. | Kane at 100°. |
|---|---|---|---|---|---|---|---|---|---|
| 18 C | 108 | 49·09 | | 14 C | 84 | 49·96 | | 49·09 | 48·86 |
| N | 14 | 6·36 | | N | 14 | 8·30 | | | |
| 10 H | 10 | 4·55 | | 7 H | 7 | 4·15 | | 5·14 | 5·43 |
| 11 O | 88 | 40·00 | | 8 O | 64 | 37·59 | | | |
| $C^{18}NH^{10}O^{11}$ | 220 | 100·00 | | $C^{14}NH^{7}O^{8}$ | 169 | 100·00 | | | |

In the mixtures of carbonic acid and nitrogen obtained by combustion, Kane found from 16·8 to 18·3 vol. carbonic acid to 1 vol. N.

According to II, azolitmin contains 2 At. oxygen more than orcein, and may be derived from orcein in the manner shown by the equation:

$$C^{14}H^{8}O^{4} + NH^{3} + 8O = C^{14}NH^{7}O^{8} + 4HO,$$

the absorption of an additional quantity of oxygen being favoured by the presence of alkaline carbonates (Gerhardt, *Traité*, 3, 818).—According to Calculation I, which

agrees best with the analyses of azolitmin and its compounds, azolitmin contains 1 At. oxygen more than according to Kane's formula $C^{18}NH^{10}O^{10}$, and 3 At. oxygen more than orcein, according to Kane's formula for that substance.

Azolitmin suspended in water through which chlorine gas is passed yields yellow chlorazolitmin.

It is sparingly soluble in water.

It dissolves readily in aqueous ammonia and potash, forming the blue of litmus. When the ammoniacal solution is left to evaporate, the greater part of the ammonia escapes; the residue does not exhibit a constant composition. Neither does the absorption of ammoniacal gas by azolitmin obey any regular law.

*Litmus* is obtained from the same lichens that yield archil, by treating them with carbonate of potash in addition to ammonia. — 30 grms. of *Roccella tinctoria:* (*a*) mixed with 5 grms. of carbonate of potash; (*b*) with 2 grms. of slaked lime; (*c*) unmixed,—were moistened during fourteen days with urine which was saturated with carbonate of ammonia and the mixture stirred several times every day; *a* yielded beautiful litmus; *b* and *c* yielded archil. — When 2 pts. of *Roccella tinctoria* and 1 pt. of carbonate of potash are repeatedly moistened with urine which is saturated with carbonate of ammonia (pure carbonate of ammonia exerts the same action), the mass acquires in 3 days a brown or dirty red colour; in 20 or 25 days, a purple-red; in 30 days a blue colour; and in 40 days yields litmus of the best quality. (Gélis, *J. Pharm.* 24, 277.) — Litmus (*tournesol en pains*) is prepared in Holland from *Lecanora tartarea* and *Roccella tinctoria* of the Canary Isles, the coloured mass obtained as above being thickened with chalk or gypsum. The colouring matter contained in it consists chiefly of azolitmin.

The ammoniacal solution of azolitmin forms with the salts of the heavy metallic oxides, precipitates which are red or blue, according to the quantity of oxide contained in them.

*Lead-compound.* — The recently precipitated compound has a beautiful violet colour but turns blue after drying at 170°.

| | | | | | | | | | | | Kane. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 3 PbO | 335·4 | .... | 60·39 | 2 PbO | 222·8 | .... | 58·29 | .... | 59·38 |
| 18 C | 108·0 | .... | 19·44 | 14 C | 84·0 | .... | 21·90 | .... | 19·08 |
| N | 14·0 | .... | 2·52 | N | 14·0 | .... | 3·65 | | |
| 10 H | 10·0 | .... | 1·80 | 6 H | 6·0 | .... | 1·56 | .... | 2·00 |
| 11 O | 88·0 | .... | 15·85 | 7 O | 56·0 | .... | 14·60 | | |
| $C^{18}NH^{10}O^{11}$,3PbO.. | 555·4 | .... | 100·00 | $C^{14}NPbO^{8}$,PbO | 382·8 | .... | 100·00 | | |

Sulphuretted hydrogen converts the compound into a black powder, which appears to be a compound of azolitmin with sulphide of lead, inasmuch as the azolitmin can be extracted from it by water only after long boiling, but is immediately dissolved out by potash or ammonia, whereas azolitmin is more soluble in water containing sulphuretted hydrogen than in pure water.

*Stannous compound.* — *a. Prepared in the cold.* — [The method is not given. L.] Has a fine violet colour. It is partially decomposed when dried by heat. It is decolorised by boiling with water, the protoxide of

tin being converted into binoxide. The greenish white compound thus formed quickly absorbs oxygen from the air, and forms a red compound of regenerated azolitmin with stannic oxide.

| | | | Kane. |
|---|---|---|---|
| 18 C | 108 | 21·34 | 20·85 |
| N | 14 | 2·77 | |
| 12 H | 12 | 2·37 | 2·84 |
| 4 Sn | 236 | 46·64 | 45·99 |
| 17 O | 136 | 26·88 | |
| $C^{18}NH^{10}O^{11},4SnO$ | 506 | 100·00 | |

*b*. Protochloride of tin forms with an ammoniacal solution of azolitmin, a beautiful violet precipitate, which must be washed and then dried at 100°.

By boiling with water slightly acidulated with hydrochloric acid, it is converted into a white compound of leucazolitmin with stannic oxide.

| | | | Kane. |
|---|---|---|---|
| 18 C | 108 | 29·03 | 29·45 |
| N | 14 | 3·76 | |
| 12 H | 12 | 3·22 | 3·55 |
| 2 Sn | 118 | 31·22 | |
| 15 O | 120 | 32·77 | 33·22 |
| $C^{18}NH^{10}O^{11},2SnO + 2Aq$ | 372 | 100·00 | |

*Stannic compound.* — The compound of leucazolitmin with stannic oxide is exposed to the air in the moist state, till it acquires a scarlet colour. This scarlet compound gives off 2 At. water (4·5 per cent.) at 140°.

| | | | Kane. |
|---|---|---|---|
| 18 C | 108 | 27·83 | 27·43 |
| N | 14 | 3·61 | |
| 12 H | 12 | 3·09 | 3·65 |
| 2 Sn | 118 | 30·41 | 31·48 |
| 17 O | 136 | 35·06 | |
| $C^{18}NH^{10}O^{11},2SnO^{2} + 2Aq$ | 388 | 100·00 | |

[From Gerhardt's formula for azolitmin, it is impossible to deduce any formula for these tin-compounds.]

Azolitmin is insoluble in alcohol.

## Chlorazolitmin.

KANE. *N. Ann. Chim. Phys.* 2, 155; *Pharm. Centr.* 1841, 574.

When chlorine is passed into water in which azolitmin is supended, a yellow substance is formed, which is insoluble in water, but dissolves in alcohol, ether and alkalis, and is precipitated from the latter in its original state by acids.

| I. | | | | II. | | | | Kane. |
|---|---|---|---|---|---|---|---|---|
| 18 C | 108·0 | .... | 42·45 | 14 C | 84·0 | .... | 41·30 | .... 42·94 |
| N | 14·0 | .... | 5·50 | N | 14·0 | .... | 6·88 | |
| 9 H | 9·0 | .... | 3·54 | 6 H | 6·0 | .... | 2·95 | .... 4·64 |
| Cl | 35·4 | .... | 13·92 | Cl | 35·4 | .... | 17·40 | .... 14·32 |
| 11 O | 88·0 | .... | 34·59 | 8 O | 64·0 | .... | 31·47 | |
| $C^{18}NClH^{9}O^{11}$ | 254·4 | .... | 100·00 | $C^{14}NClH^{6}O^{8}$ | 203·4 | .... | 100·00 | |

## Leucazolitmin.

KUHLMANN. *Ann. Chim. Phys.* 54, 291 ; *Pharm. Centr.* 1834, 646.
KANE. *N. Ann. Chim. Phys.* 2, 150; *Pharm. Centr.* 1841, 572.
VOGEL. *J. pr. Chem.* 16, 311.

Produced from azolitmin by nascent hydrogen, but cannot be prepared in the pure state, because it immediately becomes coloured by taking up oxygen from the air.

The compound of *leucazolitmin with stannic oxide* is produced by boiling the compound of azolitmin and stannous oxide with water slightly acidulated with hydrochloric acid. White or slightly yellowish powder, which by exposure to the air, is immediately converted into the scarlet compound of azolitmin with stannic oxide. (Kane.)

When tincture of litmus is mixed in a bottle completely full, with a few drops of sulphuretted hydrogen water, it is decolorised, but on exposure to the air, the liquid regains its blue colour. (Vogel.) Tincture of litmus which had been kept for several months in a closed bottle, acquired a reddish yellowish colour, and yielded sulphuretted hydrogen (perhaps arising from decomposition of sulphates), but resumed its blue colour on exposure to the air (compare Malaguti, *N. Ann. Chim. Phys.* 37, 206). In a similar manner, tincture of litmus is decolorised by hydrosulphate of ammonia or by protoxide of iron. (Kuhlmann.)

## Spaniolitmin.

KANE. *N. Ann. Chim. Phys.* 2, 140 ; *Ann. Pharm.* 39, 60; *Pharm. Centr.* 1841, 570.

From σπανιος, rare.

Sometimes obtained in the preparation of azolitmin. As there is no known method of separating these two bodies, an admixture of spaniolitmin in azolitmin is recognised by the combustion yielding more than 18 vol. carbonic acid to 1 vol. nitrogen; if the substance is free from nitrogen, it consists of spaniolitmin.

Light red.

| | *At* 100°. | | | Kane. |
|---|---|---|---|---|
| 18 C | 108 | .... | 44·44 | ..... 43·93 |
| 7 H | 7 | .... | 2·88 | ..... 3·11 |
| 16 O | 128 | .... | 52·68 | ..... 52·96 |
| $C^{18}H^{7}O^{16}$ | 243 | .... | 100·00 | ..... 100·00 |

The analysis likewise agrees with the formula $C^{26}H^{11}O^{23}$, according to which spaniolitmin should be formed from erythrolitmin by addition of 11 O; but this formula does not agree with the analysis of the lead-compound. Spaniolitmin is probably formed from azolitmin by abstraction of ammonia and addition of oxygen (Kane):

$$C^{18}NH^{10}O^{11} - NH^{3} + 5O = C^{18}H^{7}O^{16}.$$

Spaniolitmin dissolves in water with light red colour.

Alkalis turn it blue; the ammonia-compound is decomposed, though not completely, at a very gentle heat.

*Lead-compound of Spaniolitmin.* — *a.* Of a fine violet colour; after drying, it gives off 3·5 per cent of water at 121°.

| | *At* 121°. | | Kane. |
|---|---|---|---|
| 5 PbO | 559·8 | 69·70 | 70·00 |
| 18 C | 108·0 | 13·47 | 12·63 |
| 7 H | 7·0 | 0·87 | 1·09 |
| 16 O | 128·0 | 15·96 | 16·28 |
| $C^{18}H^{7}O^{16}$,5PbO | 802·8 | 100·00 | 100·00 |

*b.* In an ammoniacal solution of spaniolitmin, basic acetate of lead forms an azure-coloured precipitate which is not altered by excess of ammonia. Dried at 82°, it contains 5 per cent. (9 At.) of water, which escapes at 121°.

| | *At* 121°. | | Kane. |
|---|---|---|---|
| 12 PbO | 1341·6 | 84·67 | 84·31 |
| 18 C | 108·0 | 6·82 | 6·45 |
| 7 H | 7·0 | 0·44 | 0·43 |
| 16 O | 128·0 | 8·07 | 8·81 |
| $C^{18}H^{7}O^{16}$,12PbO | 1584·6 | 100·00 | 100·00 |

*Silver-compound.* — Of a fine purple colour. Gradually blackens when exposed to light.

| | *At* 100°. | | Kane. |
|---|---|---|---|
| 3 Ag | 324 | 54·82 | 53·92 |
| 18 C | 108 | 18·27 | 18·66 |
| 7 H | 7 | 1·18 | 1·61 |
| 19 O | 152 | 25·73 | 25·81 |
| $C^{18}H^{7}O^{16}$,3AgO | 591 | 100·00 | 100·00 |

Spaniolitmin is insoluble in *alcohol* and in *ether*.

## Alpha-orcein.

KANE. *N. Ann. Chim. Phys.* 2, 27; *Ann. Pharm.* 39, 42; *Pharm. Centr.* 1841, 566.

Orcein prepared from archil (p. 358) is very often mixed with alpha-orcein, of which however the archil contains, less in proportion as it is

older. Alpha-orcein agrees in all respects with orcein and cannot be distinguished from it excepting by the results of analysis. [How is it to be separated? L.]

| | | | Kane. |
|---|---|---|---|
| 18 C | 108 | 62·79 | 62·45 |
| N | 14 | 8·22 | |
| 10 H | 10 | 5·81 | 6·00 |
| 5 O | 40 | 23·18 | |
| $C^{18}NH^{10}O^{5}$ | 172 | 100·00 | |

*Alpha-orcein with Lead-oxide.* — An ammoniacal solution of alpha-orcein mixed with neutral acetate of lead and neutralised with acetic acid, yields a purple precipitate.

| | *At* 200°. | | Kane. |
|---|---|---|---|
| 3 PbO | 335·4 | 66·11 | 66·13 |
| 18 C | 108·0 | 21·28 | 21·29 |
| N | 14·0 | 2·76 | |
| 10 H | 10·0 | 1·97 | 2·21 |
| 5 O | 40·0 | 7·88 | |
| $C^{18}NH^{10}O^{5},3PbO$ | 507·4 | 100·00 | |

## Erythrolein.

KANE. *Phil. Trans.* 1840, 299; *N. Ann. Chim. Phys.* 2, 131; *Ann. Pharm.* 39, 32; *Pharm. Centr.* 1841, 568.

*Preparation* (p. 364). — To purify the product, it is dissolved in ether, and after a few hours, the solution is decanted and the ether driven off by the heat of the water-bath.

*Properties.* Semifluid at ordinary temperatures, perfectly fluid at 38°.

| | | | Kane. |
|---|---|---|---|
| 26 C | 156 | 74·28 | 73·24 |
| 22 H | 22 | 10·47 | 10·68 |
| 4 O | 32 | 15·25 | 16·08 |
| $C^{26}H^{22}O^{4}$ | 210 | 100·00 | 100·00 |

The quantity of oxygen varies in different analyses, but the ratio of the carbon to the hydrogen is constant.

When heated it decomposes without volatilising.

It is nearly insoluble in water, but imparts to that liquid the red colour of onions.

It dissolves in ammonical water with a splendid purple colour without a trace of blue.

With metallic oxides it forms by double decomposition beautiful violet lakes; in the lead-compound dried at 100°, the organic matter has always the same composition; but there is no simple stoïchiometric relation between the erythrolein and the lead-oxide.

Erythrolein dissolves in *alcohol* and in *ether*, forming solutions of a fine red colour.

## Erythrolitmin.

KANE. *Phil. Trans.* 1840, 301; *N. Ann. Chim. Phys.* 2, 132; *Ann. Pharm.* 39, 53; *Pharm. Centr.* 1841, 568.

*Preparation* (p. 364). It must be heated for an hour or two to 110°, in order to expel the ether completely.

*Properties.* Of a fine and pure red colour. Separates on cooling from the boiling alcoholic solution in small, dark red, crystalline grains destitute of lustre. Gives off 1 At. water at 100°.

| | | | Kane. *a.* | Kane. *b.* |
|---|---|---|---|---|
| 26 C | 156 | 55·12 | 55·01 | 54·54 |
| 23 H | 23 | 8·13 | 8·69 | 8·10 |
| 13 O | 104 | 36·75 | 36·30 | 37·36 |
| $C^{26}H^{22}O^{12}$ + HO | 283 | 100·00 | 100·00 | 100·00 |

*a* was dried at 100°; *b* at 121°.

Erythrolitmin suspended in water is converted by chlorine gas into a yellowish substance, which is insoluble in water, and when dried at 100°, contains 56·50 p.c. C, 8·18 H, and 6·85 O, corresponding to the formula $C^{52}ClH^{44}O^{10}$.

Erythrolitmin dissolves very sparingly in water, forming a red solution.

With ammonia it forms a blue compound insoluble in water, which separates when the aqueous solution is mixed with a small quantity of ammonia; when dried, it gives off ammonia and assumes a purple-red colour. — Erythrolitmin absorbs dry ammoniacal gas, with rise of temperature and loss of the second atom of water; the resulting blue compound contains 1 At. ammonia, half of which goes off at 130°, leaving a red-violet-black substance which is insoluble in alcohol, immediately turns red, like erythrolitmin, when treated with a dilute acid, and consists of $C^{26}H^{22}O^{12} + \frac{1}{2}NH^{3}$. [According to this, the atomic weight of erythrolitmin should be doubled. L.]

Erythrolitmin dissolves with blue colour in strong potash-ley.

With metallic oxides it forms lakes of a fine purple-red colour.

*Erythrolitmin with Lead-oxide.* — Erythrolitmin is boiled with alcohol, basic acetate of lead added, the liquid boiled for a while, and the dark red precipitate washed and dried at 100°.

| | | | Kane. |
|---|---|---|---|
| 2 PbO | 223·6 | 44·93 | 44·48 |
| 26 C | 156·0 | 31·35 | 30·80 |
| 22 H | 22·0 | 4·42 | 4·78 |
| 12 O | 96·0 | 19·30 | 19·99 |
| $C^{26}H^{22}O^{12}$,2PbO | 497·6 | 100·00 | 100·00 |

Erythrolitmin dissolves abundantly in *alcohol*, and a solution saturated at the boiling heat deposits part of it in the crystalline form on cooling. It dissolves very sparingly in *ether*.

*Conjugated Compounds of Orcin.*

## Orsellic Acid.

$C^{16}H^8O^8 = C^{14}H^8O^4,2C\dot{O}^2$.

STENHOUSE. *Phil. Trans.* 1848, 66; *Ann. Pharm.* 68, 61, 68. — *Phil. Mag.* 32, 300; *J. pr. Chem.* 45, 180; *Pharm. Centr.* 1848, 316.

*Alpha-orsellinsäure, Beta-orsellinsäure, Alpha-orsellesic acid, Beta-orsellesic acid, Acide orsellique.*

*Formation.* Produced from lecanoric acid by boiling with water, alcohol, or alkalis:

$$C^{32}H^{14}O^{14} + 2HO = 2C^{16}H^8O^8;$$

from erythric acid, simultaneously with picroerythrin, when the baryta or lime salt of that acid is boiled with water:

$$C^{40}H^{22}O^{20} + 2HO = C^{24}H^{16}O^{14} + C^{16}H^8O^8;$$

from evernic acid, simultaneously with everninic acid, by boiling with baryta-water:

$$C^{34}H^{16}O^{14} = C^{18}H^{10}O^8 + C^{16}H^8O^8;$$

from $\beta$-orsellic acid, simultaneously with roccellin, by boiling with water or alcohol:

$$C^{34}H^{15}O^{15} = C^{16}H^8O^8 + C^{18}H^7O^7.$$

In these reactions, the orsellic acid is often resolved into orcin and carbonic acid.

*Preparation.* When recently precipitated gelatinous lecanoric acid is exactly neutralised with baryta or lime water, and boiled till the whole is clearly dissolved, the lecanoric acid is found to be completely converted into orsellic acid; if the baryta of lime is not in excess, no separation of carbonate takes place. The cooled solution is decomposed by hydrochloric acid; and the resulting gelatinous precipitate is washed with water, dried, and crystallised from weak alcohol.—In like manner, orsellic acid may be obtained from erythric, evernic or beta-orsellic acid.

*Properties.* Crystallises from water or alcohol in long, white needles arranged in stellate groups. Tastes slightly sour and bitter. Reddens litmus distinctly.

| | | | | Stenhouse. |
|---|---|---|---|---|
| 16 C | 96 | 57·15 | | 57·95 |
| 8 H | 8 | 4·76 | | 5·17 |
| 8 O | 64 | 38·09 | | 36·88 |
| $C^{16}H^8O^8$ | 168 | 100·00 | | 100·00 |

*Decompositions.* 1. Boiled with water, it gives off carbonic acid, and is quickly converted into orcin, which is deposited from the concentrated solution in colourless crystals:

$$C^{16}H^{8}O^{6} = C^{14}H^{8}O^{4} + 2CO^{2}.$$

2. Baryta or lime-water in excess acts in a similar manner, with separation of carbonate; the orcin thus obtained is contaminated with a reddish colouring matter difficult to separate. — 3. Chloride of lime imparts to it a transient blue colour.—4. The ammoniacal solution yields on exposure to the air, a colouring matter resembling orcein.

*Combinations.* Orsellic acid dissolves in hot water more readily than lecanoric acid (p. 377).

*Orsellate of Baryta.* — The warm alcoholic solution of the acid is carefully mixed with small quantities of baryta-crystals, the acid being left slightly in excess, and the solution not neutralised completely till it has been evaporated. The syrup thus obtained crystallises on cooling in thin prisms, which dissolve very readily in water and weak alcohol; so that to obtain crystals, the aqueous solution must be evaporated in vacuo to a syrup: from weak alcohol, long four-sided prisms are obtained, which give off between 7 and 11 per cent. of water in vacuo, according to the strength of the alcohol. The salt decomposes at 100°.

| | | | Stenhouse. |
|---|---|---|---|
| BaO | 76·6 | 32·45 | 31·87 |
| 16 C | 96·0 | 40·78 | 41·29 |
| 7 H | 7·0 | 2·97 | 3·63 |
| 7 O | 56·0 | 23·80 | 23·21 |
| $C^{16}H^{7}BaO^{8}$ | 235·6 | 100·00 | 100·00 |

The acid dissolves very readily in *alcohol* whether hot or cold.

## Orsellate of Methyl.

$$C^{18}H^{10}O^{8} = C^{2}H^{3}O,C^{16}H^{7}O^{7}.$$

C. Schunck. (1845.) *Ann. Pharm.* 54, 268; *Pharm. Centr.* 1845, 727.
Stenhouse. *Ann. Pharm.* 68, 75.
Strecker. *Ann. Pharm.* 68, 111.

*Lecanorate of Methyl, Erythrate of Methyl.*

*Preparation.* Lecanoric or erythric acid is boiled for several hours with strong wood-spirit; the liquid evaporated to dryness, and the residue boiled with water; the filtrate on cooling becomes filled with needles having a silky lustre.

*Properties.* Crystallises from wood-spirit in shining crystals, from water in silky needles. (Schunck.) The crystals are generally flat-pointed or united in laminæ. (Stenhouse.) Volatile without decomposition.

| | | | Schunck, *from lecanor. ac.* | Stenhouse, *from erythrin.* |
|---|---|---|---|---|
| 18 C | 108 | 59·35 | 57·92 | 59·44 |
| 10 H | 10 | 5·49 | 5·41 | 5·61 |
| 8 O | 64 | 35·16 | 36·67 | 34·95 |
| $C^{18}H^{10}O^{8}$ | 182 | 100·00 | 100·00 | 100·00 |

The compound dissolves in alkalis and is precipitated from the solution in the form of a crystalline mass.

When the alkaline solution is boiled, wood-spirit is given off and a carbonate of the alkali is produced. (Schunck.) Exhibits with reagents the same characters as orsellate of ethyl. (Schunck, Stenhouse.)

It dissolves in water more readily than orsellate of ethyl; the excess of the orsellate of methyl melts in boiling water, forming oily drops. (Schunck.)

## Orsellate of Ethyl.

$C^{20}H^{12}O^{8} = C^{4}H^{5}O,C^{16}H^{7}O^{7}$.

HEEREN. (1830.) *Schw.* 59, 341.
LIEBIG. *Pogg.* 21, 32.
KANE. *Phil. Trans.* 1840, 237, 279; *N. Ann. Chim. Phys.* 2, 514; *Ann. Pharm.* 39, 32, 76; *Pharm. Centr.* 1841, 563.
SCHUNCK. *Ann. Pharm.* 41, 160; 54, 265.—*Phil. Mag. J.* 29. 261; *Ann. Pharm.* 61, 72; *J. pr. Chem.* 38, 456; *Pharm. Centr.* 1845, 725.
ROCHLEDER & HELDT. *Ann. Pharm.* 48, 5.
STENHOUSE. *Ann. Pharm.* 68, 74.
STRECKER. *Ann. Pharm.* 68, 111.

*Pseuderythrin* (Heeren), *Erythrin* (Kane), *Lecanoric ether* (Rochleder & Heldt), *Erythric ether* (Schunck, Stenhouse), *Orsellinvinester.*

*Formation.* By boiling orsellic, lecanoric, erythric or β-orsellic acid with alcohol. By treating an alcoholic solution of lecanoric acid with hydrochloric or sulphuric acid. (Rochleder & Heldt.)

*Preparation.* 1. *a. Roccella tinctoria* is repeatedly boiled with alcohol; the filtered extract is mixed with twice its volume of cold water, whereby a mixture of roccellin and chlorophyll is precipitated; the liquid is then heated to the boiling point; powdered chalk is added till the precipitate aggregates in white flakes easy to separate by filtration; and the liquid is filtered as quickly as possible. The filtrate does not become turbid on cooling; neither does it deposit any spongy sediment till after some days. If the liquid decanted therefrom, and the residue containing the sediment, be heated to the boiling point and quickly filtered, the liquid, on cooling, first becomes turbid, and afterwards deposits crystalline laminæ of orsellate of ethyl, the turbidity then disappearing. The crystals are purified by recrystallisation from alcohol, with addition of animal charcoal. (Heeren.) —*b.* The finely chopped lichens are repeatedly exhausted with alcohol at a temperature just below its boiling point, the mixture being each time heated in a retort for several hours. The united liquids are then distilled

to dryness over the water-bath; the yellowish residue is boiled for a few minutes with water, the hot liquid filtered as quickly as possible, and the residue boiled a few times more with water.—The aqueous solution, on cooling, deposits orsellate of ethyl in laminæ resembling boracic acid, which, if the liquid has been boiled and filtered quickly, often cause it to solidify completely; the brown mother-liquor evaporated over the water-bath yields *amarythrin* in the form of a semi-fluid extract. (Kane.) — *c.* The powder of various kinds of Lecanora or Variolaria is boiled with alcohol, the liquid evaporated to dryness, and the residue exhausted with boiling water, which on cooling deposits shining laminæ or needles. (Schunck.) — 2. Lecanoric acid, *e. g.*, the crude acid precipitated by hydrochloric acid and dried, is boiled for 6 or 8 hours with strong alcohol; the solution evaporated over the water-bath till nearly all the alcohol is expelled; the residue boiled with water; and the liquid filtered. On cooling it deposits crystals, which are coloured yellow by an adhering resin, but may be decolorised by repeated solution and boiling with animal charcoal. (Schunck, Stenhouse.) Schunck evaporates the alcoholic liquid to complete dryness; Stenhouse, on the other hand, finds that the evaporation causes decomposition of the ether, a resinous substance being formed. In the mother-liquor, Schunck found a large quantity of orcin; for purification, he boils the coloured crystals with a quantity of water not sufficient to dissolve them; the undissolved portion then melts into oily drops which retain the impurity. — 3. Erythric or $\beta$-orsellic acid is boiled with alcohol, the process being conducted as in 2. (Stenhouse.) The alcoholic solution of erythric acid is boiled for some time and water added; orsellate of ethyl then separates gradually in needles. — 4. Hydrochloric acid gas is passed to saturation into an alcoholic solution of lecanoric acid saturated at the boiling heat; the liquid heated in the water-bath till the greater part of the hydrochloric acid is expelled; and the residue washed with water, which precipitates a black-green resinous substance. This precipitate is boiled with water as long as any thing dissolves, and the liquid is filtered at the boiling heat. The filtrate deposits yellowish crystals which must be recrystallised from alcohol. (Rochleder & Heldt.)

*Properties.* Snow-white, very thin laminæ or long needles. (Heeren.) Flat needle-shaped or laminar crystals. (Stenhouse.) Laminæ or needles. The ether prepared by (2) crystallised in prisms when its alcoholic solution was left to evaporate. (Schunck.) Shining crystalline laminæ. (Rochleder & Heldt.) — Melts at a temperature a little above 120°, forming a colourless oil which on cooling forms a laminar crystalline mass. (Heeren.) Melts at 104°. (Kane.) When boiled with a quantity of water not sufficient to dissolve it, it melts into a heavy oil which solidifies in the crystalline form on cooling. (Heeren, Schunck.) The ether (prepared by 2,) melts when heated in a glass tube, and distils almost completely in the form of a liquid which soon crystallises. (Schunck.) It is tasteless at first, but produces a burning sensation on the tongue when chewed for some time. Its solutions are neutral. (Schunck, preparation 2.)

| | | | | Liebig. | Kane. |
|---|---|---|---|---|---|
| 20 C | 120 | 61·23 | | 60·00 | 60·33 |
| 12 H | 12 | 6·12 | | 6·32 | 6·25 |
| 8 O | 64 | 32·65 | | 33·68 | 33·42 |
| $C^{20}H^{12}O^{8}$ | 196 | 100·00 | | 100·00 | 100·00 |

| | | Schunck. | | | Stenhouse. | | Rochleder |
|---|---|---|---|---|---|---|---|
| | | *a.* | *b.* | *c.* | *a.* | *b.* | & Heldt. |
| 20 C | 120 | 60·83 | 60·69 | 60·68 | 61·19 | 60·80 | 60·80 |
| 12 H | 12 | 6·23 | 6·20 | 6·13 | 6·20 | 6·23 | 6·38 |
| 8 O | 64 | 32 94 | 33·11 | 33·19 | 32·61 | 32·97 | 32·82 |
| $C^{20}H^{12}O^{8}$ | 196 | 100·00 | 100·00 | 100·00 | 100·00 | 100·00 | 100·00 |

Liebig & Kane analysed the ether prepared by (1); Schunck's analysis *a* was made with the product obtained by (1); *b* with that prepared (2); *c* with the product obtained from erythric acid. Stenhouse's analysis *a* was made with the product obtained by 2; *b* with that from β-orsellic acid; Rochleder & Heldt analysed the ether prepared by 4.

*Decompositions.* 1. Orsellic ether heated on platinum-foil melts into an oil, and gives off thick suffocating vapours. — 2. It dissolves in warm nitric acid, and the liquid, if strongly heated, gives off yellowish red vapours, and is afterwards found to contain oxalic acid. (Schunck.) — The ether dissolves in fuming nitric acid, forming a dark blood-red liquid from which it is precipitated by water in its original state. (Marx, *Schw.* 60, 127.) — 3. It dissolves in oil of vitriol, and the solution when heated, assumes a dark brown colour, gives off sulphurous acid, and deposits brown flakes on being mixed with water. The cold alkaline solution becomes brown when exposed to the air. (Heeren, Kane, Schunck.) When the ether is heated with alkalis or baryta-water, alcohol distils over, and the residue contains orcin and carbonic acid. (Schunck.) The ammoniacal solution becomes red by absorption of oxygen. (Heeren, Kane, Schunck.) — 6. The aqueous or alkaline solution instantly reduces a solution of gold but a silver-solution is not reduced by it till boiled with ammonia, a metallic speculum being then formed and the solution turning red. (Schunck.)

*Combinations.* Orsellic ether dissolves very sparingly in cold, abundantly in hot water, crystallising in shining laminæ as it cools.

It dissolves in cold caustic alkalis and their carbonates, in baryta-water and in lime-water, and is precipitated without alteration by acids. It dissolves in ammonia without decomposition, if kept from contact with the air, and crystallises in slender needles when evaporated.

A solution of orsellic ether in the smallest possible quantity of ammonia forms with nitrate or acetate of lead an abundant white precipitate (Kane); it precipitates basic acetate of lead, but not the neutral acetate of lead.

| | | | Kane. |
|---|---|---|---|
| 7 PbO | 782·6 | 79·97 | 80·59 |
| 20 C | 120·0 | 12·26 | 11·73 |
| 12 H | 12·0 | 1·23 | 1·32 |
| 8 O | 64·0 | 6·54 | 6·36 |
| $C^{20}H^{12}O^{8},7PbO$ | 978·6 | 100·00 | 100·00 |

The ammoniacal solution of the ether precipitates nitrate of silver. (Compare decomposition 2.)

Orsellic ether dissolves very readily in *alcohol* and *ether*, but not in acetic acid.

*Appendix to Orsellate of Ethyl.*

## Amarythrin. $C^{22}H^{14}O^{14}$. ?

KANE. *Phil. Trans.* 1840, 282; *N. Ann. Chim. Phys.*

Produced when a solution of orsellic ether in boiling water is exposed to the air for a considerable time.

*Preparation* (p. 374).

*Properties.* Brown semifluid extract, which does not give off all its water till raised to a temperature at which it begins to decompose. Has a peculiar sweet and bitter taste. Smells like caramel.

In contact with the air, it is quickly converted into telerythrin.

It dissolves readily in water, forming a brown solution, which yields, with heavy metallic salts, red-brown precipitates of constant composition.

The lead-compound, which is obtained (*a*) by precipitating the aqueous solution with nitrate of lead, and the precipitate (*b*) produced on neutralising the liquid filtered from *a*, have the same composition.

| | | | Kane. | |
|---|---|---|---|---|
| | | | *a.* | *b.* |
| 2 PbO | 223·6 | 46·42 | 45·62 | 45·90 |
| 22 C | 132·0 | 27·41 | 27·46 | 27·13 |
| 14 H | 14·0 | 2·91 | 2·96 | 2·72 |
| 14 O | 112·0 | 23·26 | 23·96 | 24·25 |
| $C^{22}H^{14}O^{14}$,2PbO | 481·6 | 100·00 | 100·00 | 100·00 |

Amarythrin dissolves sparingly in alcohol, but is insoluble in ether.

## Telerythrin. $C^{22}H^{10}O^{20}$. ?

KANE. *Phil. Trans.* 1840, 283; *N. Ann. Chim. Phys.* 2, 19; *Ann. Pharm.* 39, 36; *Pharm. Centr.* 1841, 564.

A concentrated aqueous solution of amarythrin exposed to the air for several months, changes into a brownish crystallo-granular mass, which, when freed from adhering amarythrin by hot alcohol, becomes nearly white. Has a sweetish bitter taste. Neutral. After drying in the air, it does not give off any water when heated.

| | | | Kane. |
|---|---|---|---|
| 22 C | 132 | 43·70 | 44·45 |
| 10 H | 10 | 3·31 | 3·72 |
| 20 O | 160 | 52·99 | 51·83 |
| $C^{22}H^{10}O^{20}$ | 302 | 100·00 | 100·00 |

The ammoniacal solution changes on exposure to the air less quickly than that of erythric acid, but ultimately assumes a dark wine-red colour.

Telerythrin dissolves very readily in water. The solution forms nearly white precipitates with the salts of the heavy metals. The precipitate formed with basic acetate of lead, has, after drying at 100°, the composition $C^{28}H^{9}O^{18},5PbO$.

It dissolves sparingly in *alcohol*, but is insoluble in *ether*.

## Lecanoric Acid.

$$C^{32}H^{11}O^{14} = C^{16}H^{7}O^{7},C^{16}H^{7}O^{7}.*$$

SCHUNCK. (1842.) *Phil. Mag. J.* 20, 495; *Ann. Pharm.* 41, 157; *Pharm. Centr.* 1842, 139.—*Ann. Pharm.* 54, 261; *Pharm. Centr.* 1845, 721.—*Ann. Pharm.* 61, 72.—*Phil. Mag. J.* 33, 257.
ROCHLEDER & HELDT. *Ann. Pharm.* 48, 2.—*Pharm. Centr.* 1844, 49.
STENHOUSE. *Phil. Trans.* 1848, 64; *Ann. Pharm.* 68, 59; *Pharm. Centr.* 1848, 316.
STRECKER. *Ann. Pharm.* 68, 112; *Pharm. Centr.* 1849, 119.
GERHARDT. *Compt. chim.* 1849, 128.

*Alpha-orsellic acid, Lecanorin.*

*Sources.* In various lichens of the genera *Lecanora, Variolaria, &c.*

*Preparation.* 1. The finely divided plants are exhausted with ether in a displacement apparatus; the ether distilled off; and the greyish yellow residue washed in a large funnel with cold ether, as long as the ether is coloured by it, then boiled with water to remove the orsellate of ethyl which has been formed, and recrystallised from warm alcohol.—If the acid thus obtained is contaminated with parellic acid, the mixture must be treated with baryta-water, the dissolved lecanorate of baryta filtered from the insoluble parellate, and the solution decomposed with hydrochloric acid. (Schunck.) — 2. *Evernia Prunastri* is covered with a mixture of ammonia and hydrated alcohol in a vessel which can be closed; and the liquid after a few minutes is strained through a cloth, washed with ⅓ its bulk of water and neutralised with acetic acid. The acid is then precipitated in green flakes, which are washed with cold water by decantation, dried at 100°, and crystallised from a small quantity of boiling alcohol. The precipitate is sometimes contaminated with a body insoluble in ether, to remove which, it must be digested in ether and the ether distilled from the filtrate. (Rochleder & Heldt.) — 3. Chopped *Roccella tinctoria* is macerated for a few hours with a considerable quantity of water; an excess of slaked lime added; the whole well stirred round, and left to settle; and the clear pale yellow liquid decanted and filtered. The residue is mixed with half its weight of water, the liquid expressed after a quarter of an hour, and both extracts supersaturated with hydrochloric acid; and the white gelatinous precipitate is washed by decantation, collected on linen, immediately dried on a plate of gypsum, and dissolved in warm (not boiling) alcohol, whence the acid crystallises on cooling.

* = $2C^{16}H^{8}O^{8} - 2HO$.

If the first crystallisation is not quite colourless, it must be redissolved and digested with animal charcoal. — Lecanoric acid cannot be advantageously prepared by boiling with water, inasmuch as a large portion of it is thereby decomposed, and the resulting acid, even after repeated crystallisation from alcohol, is not quite free from a resinous and a fatty substance, from which it can be freed only by treatment with lime or baryta-water. (Stenhouse.)

*Properties.* White needles united in radiating groups. Inodorous and tasteless. Reddens litmus.

| | | | Schunck. | | Rochleder & Heldt. | Stenhouse. |
|---|---|---|---|---|---|---|
| 32 C | 192 | 60·37 | 59·90 | 59·92 | 59·45 | 60·59 |
| 14 H | 14 | 4·40 | 4·57 | 4·60 | 4·40 | 5·00 |
| 14 O | 112 | 35·23 | 35·53 | 35·48 | 36·15 | 34·41 |
| $C^{32}H^{14}O^{14}$ | 318 | 100·00 | 100·00 | 100·00 | 100·00 | 100·00 |

According to Schunck, it is $C^{16}H^{8}O^{18}$; according to Stenhouse, $C^{32}H^{16}O^{4}$; Gerhardt gave the formula $C^{32}H^{14}O^{14}$, which explains the conversion into orsellic acid.

*Decompositions.* 1. By dry distillation the acid yields a viscid distillate which soon solidifies into a radiating mass of orcin and leaves a small quantity of charcoal. (Schunck, Rochleder & Heldt, Stenhouse.) Heated on platinum-foil, it burns with a yellow flame without leaving any residue. (Stenhouse.) — 2. Boiled with water it yields orsellic acid, which by continued boiling is converted into orcin. (Schunck, Rochleder & Heldt, Strecker):

$$C^{32}H^{14}O^{14} + 2HO = 2C^{16}H^{8}O^{4}.$$

The acid boiled with alcohol yields orsellate of ethyl. — 3. By continued boiling with potash, ammonia, baryta or lime-water, it yields orcin and a carbonate of the alkali (Schunck, Rochleder & Heldt); it yields in the first instance orsellic acid, which, by further decomposition, is resolved into carbonic acid and orcin. (Stenhouse, Strecker.) — 4. When moistened with dilute sulphuric acid and left in a warm place, it is completely converted into orcin. (Schunck.) — 5. When boiled with nitric acid, it emits red fumes and the resulting syrup contains a large quantity of oxalic acid. (Schunck, Rochleder & Heldt.) — 6. With chloride of lime, it immediately assumes a deep red colour, which however quickly changes to brown and yellow, and completely disappears, if the chloride of lime has been added in excess. In this reaction, a dark green substance is also formed by oxidation of the lecanoric acid.—The colouring is produced, even when a dilute solution of chloride of lime is poured into an alcoholic or alkaline extract of the lichens. — 7. The solution of lecanoric acid in caustic ammonia assumes on exposure to the air a splendid red colour, ultimately changing to purple-red. (Schunck, Rochleder & Heldt, Stenhouse.) — 8. The ammoniacal solution forms with nitrate of silver a white precipitate which is reduced when heated, with formation of a metallic speculum. The solution of the acid in potash reduces terchloride of gold with the aid of heat. (Schunck.)

*Combinations.* Lecanoric acid dissolves in 2500 pts. of boiling water and separates in crystals on cooling. The gelatinous acid separated from the salts contains 1 At. water intimately combined, which escapes after several hours heating to 110°. (Schunck.)

It neutralises alkalis and forms with them soluble crystallisable salts; it expels carbonic acid from alkaline carbonates. (Schunck, Stenhouse.)

*Lecanorate of Baryta.* — When the acid is dissolved in a very slight excess of baryta-water, carbonic acid passed through the liquid, the solution filtered, and the precipitate, consisting of carbonate and lecanorate of baryta, exhausted with hot alcohol, the solution on cooling deposits shining slender needles united in stars. (Stenhouse.) In the solution of the acid in baryta-water, alcohol produces a yellow jelly which is not decomposed by boiling with the alcoholic liquid, and afterwards dissolves completely in water. (Schunck.)

| | *Crystallised.* | | Stenhouse. |
|---|---|---|---|
| BaO | 76·6 | 19·73 | 19·49 |
| 32 C | 192·0 | 49·87 | 49·27 |
| 13 H | 13·0 | 3·37 | 3·81 |
| 13 O | 104·0 | 27·03 | 27·43 |
| $C^{32}H^{13}BaO^{14}$ | 385·6 | 100·00 | 100·00 |

The acid acts with lime-water in the same manner as with baryta-water. (Schunck.) The ammoniacal solution forms with chloride of calcium a gelatinous precipitate sparingly soluble in water and in alcohol.

*Lecanorate of Lead.* — When solutions of lecanoric acid and neutral acetate of lead are mixed at the boiling heat, a white precipitate is formed which is somewhat soluble in alcohol, and after washing with alcohol, contains 37·7 p. c. carbon and 2·75 p. c. hydrogen. (Rochleder & Heldt.) [It appears to contain orsellate of lead. (Gerhardt, *Tr.* 3, 800.)] An alcoholic solution of lecanoric acid does not precipitate neutral acetate of lead. (Schunck.) It precipitates the basic acetate of lead but not the neutral acetate. (Stenhouse.)

An alcoholic solution of lecanoric acid is coloured dark purple red by a drop of *ferric* hydrochlorate; water added to the liquid throws down a light purple precipitate. Ferrous salts mixed with a large quantity of lecanoric acid are not precipitated by ammonia in the cold; but on boiling the dark yellow liquid, a brown precipitate of *ferric lecanorate* is produced. (Schunck.)

The alcoholic solution of the acid added to an alcoholic solution of *cupric acetate*, produces after a while a light apple-green precipitate. It does not precipitate mercuric chloride, nitrate of silver or chloride of gold. (Schunck.) With ammonio-nitrate of silver, it forms a precipitate which soon decomposes. (Stenhouse.)

Lecanoric acid dissolves in boiling acetic acid more readily than in boiling water, and crystallises in slender needles on cooling.

It dissolves in 150 pts. of 80 per cent. *alcohol* at 15·5°, and in 45 pts. of boiling alcohol, forming orsellate of ethyl; it dissolves in 80 pts. of ether at 15·5. (Schunck.)

## Picroerythrin.

$C^{24}H^{14}O^{14} = C^{16}H^{7}O^{7},C^{8}H^{9}O^{7}$.*

HEEREN. (1830.) *Schw.* 59, 325.
SCHUNCK. *Phil. Mag. J.* 29, 261; *J. pr. Chem.* 38, 449; *Ann. Pharm.* 61, 75.—*Phil. Mag. J.* 33, 253.
STENHOUSE. *Phil. Trans.* 1848, 75.—*Ann. Pharm.* 68, 76.
STRECKER. *Ann. Pharm.* 68, 110.
LAURENT. *Compt. rend.* 31, 355.

*Erypicrin.*—Prepared by Heeren in the impure state as *Erythrin-bitter.*

*Formation.* By boiling erythric acid with water:

$$C^{40}H^{22}O^{20} + 2HO = C^{24}H^{17}O^{11} + C^{16}H^{8}O^{6}.$$

Heeren considers the presence of alkalis to be necessary.

*Preparation.* 1. When erythric acid is treated for a short time with boiling water, and the liquid evaporated, a brown, glutinous, bitter-sweet mass is obtained, which gradually becomes crystalline, and after washing with water, yields pure white picroerythrin. (Schunck.)—2. Erythric acid is neutralised with baryta-water or lime-water, the liquid boiled for some time, and the resulting orsellic acid separated by hydrochloric acid; the mother-liquor, after being considerably concentrated by evaporation, yields in the cold, after a few days, yellowish crystals of picroerythrin, which are washed with cold water, and recrystallised from hot water. (Stenhouse.)—3. The light brown mother-liquor obtained in the preparation of erythric acid (p. 382, 2) yields when evaporated, a gummy residue having a bitter-sweet taste. On treating this residue with cold water, a light brown crystalline mass is left, which is to be washed with cold and dissolved in boiling water containing a little animal charcoal; the solution, filtered from the charcoal, yields after evaporation, yellowish crystalline picroerythrin, which becomes white when washed with cold water. (Schunck.)

*Properties.* Long colourless needles arranged in stellate groups (Stenhouse); white crystalline mass (Schunck). Has a peculiar sweet and strongly bitter taste. (Schunck.) Reddens litmus slightly. (Schunck.)

| | | | Schunck. | Stenhouse. |
|---|---|---|---|---|
| 24 C | 144 | 52·94 | 52·51 | 53·15 |
| 16 H | 16 | 5·88 | 6·08 | 6·01 |
| 14 O | 112 | 41·18 | 41·41 | 40·84 |
| $C^{24}H^{16}O^{14}$ | 272 | 100·00 | 100·00 | 100·00 |

According to Gerhardt, it is $C^{30}H^{30}O^{16}$, which requires 54·8 p.c. carbon (*Traité*, 3, 794).

*Decompositions.* 1. The compound melts when heated in a glass tube and yields a sublimate of orcin. It burns with a bright flame and with-

* $= C^{16}H^{8}O^{6} + C^{8}H^{10}O^{8} - 2HO$.

out residue. (Schunck.) — 2. Picroerythrin is not altered by boiling with water (Schunck); only a very small quantity of orcin (and perhaps also of erythroglucin, was formed after 36 hours' boiling. (Stenhouse.) — 3. Boiled with excess of alkali, baryta or lime, it yields orcin, erythroglucin and carbonic acid. (Stenhouse, Schunck, *Phil. Mag. J.* 33, 253);

$$C^{24}H^{16}O^{14} + 2HO = C^{14}H^{8}O^{4} + C^{8}H^{10}O^{8} + 2CO^{2}.$$

4. The ammoniacal solution quickly turns red on exposure to the air. (Heeren, Kane, Schunck, Stenhouse.) — 5. With chloride of lime it produces a blood-red colour, which quickly changes to brown and yellow. (Stenhouse.) — 6. Boiled with nitric acid, it is decomposed, with formation of nitrous acid. — 7. It dissolves in oil of vitriol, and the solution gives off sulphurous acid when heated. (Schunck.) — 8. Nitrate of silver is not precipitated by the aqueous solution, and on boiling the liquid, the glass becomes covered with a silver speculum. Solution of gold boiled with picroerythrin, is decomposed, the gold being separated in metallic scales, or, if potash be added, in the form of a black powder. (Schunck.)

*Combinations.* 1. Picroerythrin dissolves sparingly in cold, readily in hot water.

The alcoholic solution imparts a deep purple-red colour to ferric salts; but the colour is destroyed by ammonia which completely precipitates the ferric oxide.

With aqueous picroerythrin and neutral acetate of lead, Schunck obtained no precipitate; but the basic acetate yielded a precipitate containing 68·94 p. c. oxide of lead. Stenhouse could not in any way obtain a lead-compound of constant composition.

Picroerythrin dissolves in *alcohol* and in *ether*. It does not yield any compound ether by boiling with alcohol. (Schunck.)

## Erythric Acid. $C^{40}H^{22}O^{20}$.*

Fr. Nees v. Esenbeck. (1829.) *Br. Arch.* 16, 135.
Heeren. *Schw.* 59, 313.
Kane. *Phil. Trans.* 1840, 277; *N. Ann. Chim. Phys.* 2, 11; *Ann. Pharm.* 39, 31.
Schunck. *Phil. Mag. J.* 29, 261; *J. pr. Chem.* 38, 449; *Ann. Pharm.* 61, 64.
Stenhouse. *Phil. Trans.* 1840, 72; *Ann. Pharm.* 68, 72.
Strecker. *Ann. Pharm.* 68, 111.

First obtained by N. v. Esenbeck, as a "remarkable resin" from *Lecanora tartarea*; by Heeren (1830) in a state of greater purity and described as *Erythrin;* analysed in the impure state by Kane as erythrilin.

Occurs in greatest abundance in *Roccella Montagnei* (regarded by Schunck as *R. tinctoria*, var. *fuciformis*). (Stenhouse.)

$$* = 2C^{16}H^{8}O^{8} + C^{16}H^{10}O^{8} - 4HO.$$

*Preparation.* From *Roccella Montagnei.* 1. The lichen is treated with milk of lime, and the process conducted as in the preparation of lecanoric acid (p. 375). The quantity of crude acid obtained amounts to 12·1 per cent of the lichen used. (Stenhouse.) 2. The chopped lichen is boiled for some time with water in a capacious vessel, and the yellow liquid strained through a cloth; on cooling, it deposits white flakes and crystals, which are washed with cold and dissolved in hot water. The solution separated by filtration from the scanty black or brown residue deposits on cooling white crystals of erythric acid. (1 lb. of lichen yields 60 grms. of erythric acid.) (Schunck.) — 3. The lichen is digested for some time with alcohol (if the digestion be too long continued, or if the liquid be boiled, the erythric acid is decomposed and orsellic ether is formed); the liquid is filtered; and the filtrate treated as in the first mode of preparation of orsellic ether (p. 373). The filtered liquid obtained after addition of chalk deposits the erythric acid on cooling, in the form of a fine powder, which is purified by dissolving it in slightly warmed alcohol, and leaving it for some hours in contact with animal charcoal, the whole being frequently shaken; on subsequently mixing the solution with 1½ times its volume of cold water, the erythric acid separates out. (Heeren.) — 4. The lichen is immersed in a small quantity of cold strong ammonia, and kneaded with it for some time; the turbid reddish solution thus obtained is diluted with water; chloride of barium previously mixed with ammonia is added to precipitate roccellic acid; the solution filtered through good filtering paper; and the filtrate decomposed with hydrochloric acid, added in sufficient quantity to produce a slight acid reaction. The sudden separation of the erythric acid converts the liquid into a yellowish jelly, but the acid redissolves when the liquid is heated, and separates in the pulverulent form on cooling. Purification as in the second method. (Heeren.)

From *Lecanora tartarea,* the erythric acid is less easily separated by ammonia. The lichen is digested with alcohol; the alcoholic tincture mixed with water; and the precipitate treated with ether, which dissolves chlorophyll and roccellic acid and leaves impure erythric acid. (Heeren.)

*Properties.* Colourless, short, slender needles, or powder composed of microscopic spherules. (Heeren.) From the boiling alcoholic solution, it separates in stellate groups on cooling. (Schunck.) Water precipitates it from the alcoholic solution in the form of a jelly. Inodorous and tasteless. (Stenhouse.) At a temperature somewhat above 100°, it melts into a transparent gummy mass which becomes hard and brittle on cooling. (Heeren, Kane.)

It reddens litmus (Schunck); it does not. (Stenhouse.)

| | | | Stenhouse. |
|---|---|---|---|
| 40 C | 240 | 56·87 | 56·98 |
| 22 H | 22 | 5·21 | 5·51 |
| 20 O | 160 | 37·92 | 37·51 |
| $C^{40}H^{22}O^{20}$ | 422 | 100·00 | 100·00 |

Schunck assumes the formula $C^{34}H^{19}O^{15}$; Strecker doubles Stenhouse's formula $C^{20}H^{11}O^{10}$, in order to explain the decomposition by water. Gerhardt adopts the formula $C^{30}H^{16}O^{15}$, which does not explain the decomposition so well.

*Decompositions.* 1. The acid heated in a glass tube froths up, yields an oily sublimate of orcin and ultimately become carbonised. (Heeren,

Schunck.) — 2. In contact with the air, it burns without residue and with a bright sooty flame. (Heeren, Schunck.) — 3. It dissolves in *nitric acid*, with evolution of nitrous vapours, and forms a yellow liquid, which assumes an orange-colour on addition of ammonia. (Heeren.) — 4. It is dissolved by oil of vitriol without charring, but is not precipitated by water in its original state, inasmuch as the precipitate forms a brown-red pigment with ammonia on exposure to the air. (Heeren.) — 5. With chloride of lime it assumes a deep red colour, quickly changing to brown and yellow. (Stenhouse.) — 6. When boiled with water, it forms picroerythrin. (Schunck.) — 7. On boiling the solution neutralised with baryta or lime, the acid is resolved into orsellic acid and picroerythrin:

$$C^{40}H^{22}O^{20} + 2HO = C^{24}H^{16}O^{14} + C^{16}H^{8}O^{8}.$$

According to Stenhouse, the products of this decomposition are picroerythrin and erythrin, which crystallise in micaceous laminæ, and *erythritic acid* which has a strongly bitter taste; this latter substance was resolved by boiling with water, into carbonic acid and orcin and probably consisted of impure orsellic acid (compare Strecker.) [The evolution of carbonic acid which, according to Stenhouse, accompanies the formation of picroerythrin from erythric acid, is explained according to Gerhardt's formula, by the equation: $C^{32}H^{16}O^{16} + 4HO = 2CO^{2} + C^{30}H^{20}H^{16}$ (Gerhardt's picroerythrin); as however the decomposition of erythric acid likewise produces orsellic acid, which when boiled with water, is immediately resolved into carbonic acid and orcin, the carbonic acid appears rather to be the result of a secondary decomposition. L.] Erythric acid boiled with excess of lime or baryta, yields the products of decomposition of picroerythrin. (Schunck, Stenhouse.) — 8. In contact with caustic ammonia, or more slowly with carbonate of ammonia, and exposed to the air, it gradually assumes a dark wine-red colour (Heeren); purple-red (Schunck). Heeren's erythrin thus treated yields, in addition to lichen-red, which dissolves with violet colour in alkalis, a brownish-yellow substance, and a pigment which does not turn violet in contact with potash, but yields lichen-red when heated. — 9. Erythric acid boiled with wood-spirit or alcohol yields orsellate of methyl or orsellate of ethyl. (Stenhouse, Strecker.) — 10. The alcoholic solution forms with sesquichloride of iron, a purple-red mixture, which is turned yellow by ammonia, but without precipitation of ferric oxide in the cold. Gold-solution is not reduced by it, even at the boiling heat.

*Combinations.* 1. Erythric acid dissolves in 240 pts. of boiling water, and separates for the most part on cooling in flakes or as a crystalline powder. (Schunck.) It dissolves in 170 pts. of boiling water, and separates as soon as the temperature sinks a little. It is insoluble in strong boiling hydrochloric acid, but dissolves with tolerable facility in boiling acetic acid, and easily, without alteration, in cold solutions of caustic and carbonated alkalis, forming a colourless liquid. (Heeren.)

The alcoholic solution of erythric acid forms with an alcoholic solution of neutral acetate of lead a white precipitate of variable constitution. (Stenhouse.) — Schunck found in it 59·14 per cent of PbO, 27,33 C and 2·15 H. — The alcoholic solution of the acid is not precipitated by neutral acetate of lead. (Schunck.)

The alcoholic solution does not precipitate nitrate of silver, but on addition of ammonia, a white precipitate is formed, which turns black on boiling, and deposits a specular coating on the glass. (Schunck.)

The acid dissolves in *alcohol*, especially when heated and in *ether*. (Schunck.)

Erythrin dissolves in 2·29 pts. of boiling alcohol of sp. gr. 0·81 in 32·5 pts. at 12°, but is insoluble in ether (Heeren).

*Appendix to Erythric Acid.*

## Erythrilin.

KANE. *Phil. Trans.* 1840, 277; *N. Ann. Chim. Phys.* 2, 11; *Ann. Pharm.* 39, 31; *Pharm. Centr.* 1843, 562.

*Preparation.* The residue insoluble in water of the alcoholic extract of *Roccella tinctoria* (p. 373), is almost completely dissolved by digestion with potash-ley at 36°; and the filtered solution slightly supersaturated with hydrochloric acid yields a copious greenish yellow precipitate, which must be completely freed from acid by washing with water, then dissolved in slightly ammoniacal water, and the solution decomposed with chloride of barium and filtered. The greenish yellow filtrate supersaturated with hydrochloric acid, deposits *erythrilin;* the small precipitate formed with chloride of barium, yields, when treated with hydrochloric acid, *roccellin,* $C^{18}H^{7}O^{7}$.

*Properties.* When recently prepared, it is pale yellow, generally however with a greenish tinge arising from the presence of chlorophyll. Melts somewhat above 100°. Does not appear to be acid.

| | | | Kane. |
|---|---|---|---|
| 22 C | 132 | 67·35 | 66·52 |
| 16 H | 16 | 8·16 | 8·25 |
| 6 O | 48 | 24·49 | 25·23 |
| $C^{22}H^{16}O^{6}$ | 196 | 100·00 | 100·00 |

[Probably nothing but impure erythric acid.]

Decomposes a little above 100°, not any portion volatilising undecomposed.

By boiling with water, it is converted into picroerythrin.

It is insoluble in water.

It dissolves readily in alkaline liquids, but without neutralising them, and is precipitated from the solution by acids.

It combines, by double decomposition, with metallic oxides, forming compounds which, for the most part, have a green colour.

Its solution in the smallest possible quantity of ammonia forms, with nitrate of lead, a pale green pulverulent precipitate, which when washed and dried at 100°, is $C^{22}H^{16}O^{6},2PbO$.

Erythrilin dissolves in alcohol and in ether.

*Addendum to Erythric Acid.*

## Erythroglucin. $C^8H^{10}O^6$.

STENHOUSE. *Phil. Trans.* 1848, 76; 1849, 399; *Ann. Pharm.* 68, 78; 70, 225.
STRECKER. *Ann. Pharm.* 68, 111.
SCHUNCK. *Phil. Mag. J.* 7, 33, 254.
LAMY. *N. Ann. Chim. Phys.* 35, 138; abstr. *N. J. Pharm.* 22, 43; *Ann. Pharm.* 84, 369; *J. pr. Chem.* 57, 21; *Pharm. Centr.* 1853, 302. — Further: *N. Ann. Chim. Phys.* 51, 232.
R. WAGNER. *J. pr. Chem.* 61, 125.

***Pseudoorcin, Eryglucin, Erythromannite, Phycite.***

*Source.* In *Protococcus vulgaris.*

*Formation.* By boiling erythric acid or picroerythrin with excess of baryta or lime (p. 382).

*Preparation.* 1. The extract of *Lecanora Montagnei* (p. 382) obtained with milk of lime, is boiled down in an open pan to about one-third or one-fourth; carbonic acid passed into the cooled liquid as long as a precipitate continues to form; and the solution, after filtration, evaporated to a syrup over the water-bath. This syrup consists chiefly of orcin and erythroglucin, mixed with a rather large quantity of red colouring matter and a resinous substance. The orcin and the greater part of the colouring matter are extracted by cold ether; or the syrup is mixed with three times its volume of strong alcohol, from which, after a while, the erythroglucin separates in small crystals. These are collected on a cloth filter, pressed, washed with cold strong alcohol, which dissolves the orcin and the greater part of the colouring matter, and recrystallised two or three times from hot alcohol. — 2. *Protococcus vulgaris* is boiled for some hours with water, and the filtered and decolorised solution is evaporated to a syrup, precipitated with alcohol or basic acetate of lead, and the filtrate left to crystallise. — Or, 1 lb. of *Protococcus vulgaris* is digested at a temperature between 50° and 100°, with 2 lbs. of alcohol of 85°; the liquid decanted; the green residue strongly pressed out; the liquid again filtered; and the alcohol distilled to one-half. The mother-liquor of the phycic acid which is deposited on cooling, separates, when the liquid is again heated, into two layers, the alcohol at the same time evaporating. The upper layer is strongly coloured; the lower, which is less coloured, yields by evaporation a crystalline mass saturated with a black syrup, which must be pressed between fine linen, washed with very cold water, and recrystallised from hot water. (Lamy.)

*Properties.* Large colourless transparent crystals having an adamantine lustre and belonging to the right prismatic system. *Fig.* 29, often with hemihedral development of an 8-sided pyramid ($P . \infty P\infty . \frac{3P3}{2}$.) $e : e$ $(P : P) = 123° 43'$; $e : q$ $(P : \infty P\infty) = 109° 29$; $3P3 : \infty P\infty =$

138° 42′. (Miller.) Large rectangular prisms acuminated with several faces (Lamy); according to Lamy's later determinations, they belong to the square prismatic system, crystals cut at right angles to the axis of the prism, exhibiting with polarised light the system of coloured rings peculiar to crystals with one optic axis. (*N. Ann. Chim. Phys.* 51, 234; see this memoir for details of the crystalline form.) Sp. gr. 1·59. (Lamy.) Its taste is very sweet and cooling. (Lamy.) Index of refraction =1·545. (Stenhouse.) Does not exhibit circular polarisation. (Lamy.) Melts at 112° without giving off water, and volatilises partly undecomposed. (Lamy.) Does not act on litmus. — Its taste is sweet, but less so than that of orcin. It does not lose water at 100°. (Stenhouse.)

| | | | Stenhouse. | Schunck. | Lamy. | |
|---|---|---|---|---|---|---|
| 8 C | 48 | 39·34 | 39·42 | 39·68 | 39·10 | 39·22 |
| 10 H | 10 | 8·20 | 8·48 | 8·60 | 8·23 | 8·27 |
| 8 O | 64 | 52·46 | 52·10 | 51·72 | 52·67 | 52·51 |
| $C^{8}H^{10}O^{8}$ | 122 | 100·00 | 100·00 | 100·00 | 100·00 | 100·00 |

Stenhouse gave the empirical formula $C^{10}H^{12}O^{10}$; according to Gerhardt's formula $C^{14}H^{16}O^{12}$ + Aq, which requires 4·09 p. c. C, erythroglucin should be = orcin + 8HO. Lamy deduces from his own analyses the formula $C^{12}H^{15}O^{12}$, which requires 39·33 p. c. C, 6·40 H and 52·42 O. The same formula was obtained by Berthelot (*Compt. rend.* 41, 452).

*Decompositions.* 1. Erythroglucin subjected to dry distillation gives off an odour of burnt sugar, and yields a liquid which does not crystallise on cooling, but dissolves in water and in alcohol. (Stenhouse.) It begins to boil at 160° without perceptible decomposition, giving off an odour of burnt flour; as the decomposition advances, the boiling point gradually rises to about 200°, but the mass does not swell up: the residue in the retort consists partly of unaltered erythroglucin [phycite], partly of a substance analogous to glucose and possessing the power of reducing copper-salts, a property not exhibited by erythroglucin [phycite]. Erythroglucin thrown on red-hot coals gives off the odour of burnt sugar. (Lamy.) — It burns on platinum-foil with a blue flame and an odour of caramel. (Stenhouse.) — 2. It is not altered by potash, ammonia, bromine or chloride of lime. (Stenhouse, Lamy.) — 3. Fuming nitric acid converts it into nitro-erythroglucin; on heating the mixture, oxalic acid is produced. (Stenhouse.) Erythroglucin dissolves in cold oil of vitriol; the crystalline compound yields a soluble baryta-salt. It is not blackened by cold oil of vitriol, but turns brown on the application of heat. — 4. It is not fermentable. (Stenhouse, Lamy.)

*Combinations.* Erythroglucin dissolves very readily in water. The aqueous solution yields the finest crystals. (Stenhouse.)

It does not precipitate neutral or basic acetate of lead, copper-salts, or ammonio-nitrate of lead. (Stenhouse.)

It dissolves sparingly in cold *alcohol*, but is insoluble in ether. (Stenhouse.)

## Nitro-erythroglucin.

$C^8N^4H^6O^{24} = C^8X^4H^6O^8$.

STENHOUSE. *Phil. Trans.* 1849, 399; *Ann. Pharm.* 70, 225; *Pharm. Centr.* 1849, 627.

Pulverised erythroglucin added by small portions to fuming nitric acid which is kept cool, dissolves quickly with considerable rise of temperature; and if the solution be mixed with a quantity of oil of vitriol equal in weight to the nitric acid, or rather more, the whole forms in half an hour a crystalline magma which is collected on a funnel plugged with asbestos, washed with cold water, pressed between paper, and recrystallised from hot alcohol. The compound is not obtained by dissolving erythroglucin in nitrosulphuric acid and adding water.

Large shining crystalline laminæ. Melts at 61°, and solidifies in the crystalline form at a temperature a few degrees lower.

| | | | | Stenhouse. |
|---|---|---|---|---|
| 8 C | 48 | 15·89 | | 16·62 |
| 4 N | 56 | 18·54 | | 17·83 |
| 6 H | 6 | 1·99 | | 2·48 |
| 24 O | 192 | 63·58 | | 63·07 |
| $C^8N^4H^6O^{24}$ | 302 | 100·00 | | 100·00 |

Gerhardt's formula $C^{14}X^6H^{10}O^{12}$ requires 18·02 p. c. carbon.

The compound takes fire when strongly heated and burns with a bright flame. The crystals thoroughly dried and mixed with sand detonate violently under the hammer.

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*Oxygen-nucleus* $C^{14}H^8O^4$.

## Catechin.

$C^{14}H^8O^6 = C^{14}H^8O^4,O^2$.

RUNGE. *Fechner's Repertorium d. org. Chemie.* Tabelle zu. s. 606.
FR. NEES V. ESENBECK. *Repert.* 27, 211; 33, 169; 43, 337; 45, 457; *Pharm. Centr.* 1830, 43; 1831, 417.
DÖBEREINER. *Schw.* 61, 378; *Pharm. Centr.* 1831, 204.
WINCKLER. *Repert.* 59, 39; *Pharm. Centr.* 1837, 740.
BÜCHNER. *Pogg.* 39, 162.
PFAFF. *Mittheilungen*, 1, 110.
DAHLSTRÖM. *Pogg.* 39, 163; *Berzelius Jahresber.* 14, 235; *Pharm. Centr.* 1836, 201.
SVANBERG. *Pogg.* 39, 169; *Pharm. Centr.* 1836, 884.
WACKENRODER. *Ann. Pharm.* 31, 72; 37, 306; *Pharm. Centr.* 1839, 623; 1841, 401.
ZWENGER. *Ann. Pharm.* 37, 320; *Pharm. Centr.* 1841, 408.

R. HAGEN. *Ann. Pharm.* 37, 326; *Pharm. Centr.* 1841, 414.
J. T. COOPER. *Phil. Mag. J.* 24, 500; *Pharm. Centr.* 1844, 159.
GUIBOURT. *N. Ann. Chim. Phys.* 11, 360; 12, 186.
DELFFS. *Jahrb. pr. Pharm.* 12, 164; *Pharm. Centr.* 1846, 604.
NEUBAUER. *Ann. Pharm.* 96, 337; *Chem. Gaz.* 1856, 126.

***Katechin, Katechugerbesalz, Katechusäure, Tanningensäure.***

*Sources.* In *Catechu*, the aqueous extract of the wood of *Acacia Catechu* (Bombay catechu), or of the nut of *Arecca Catechu* and *Arecca guvaca* (Colombo and Bengal catechu); in *Gambir*, the extract of *Nauclea Gambir;* in *Kino*, the exudations of *Pterocarpus erinaceus*, &c.

*Formation.* By exposing the aqueous solution of catechutannic acid to the air. (Delffs.) According to Neubauer, on the contrary, catechutannic acid is formed by the oxidation of catechin.

*Preparation.* 1. Bengal or Gambir catechu is exhausted with ether in a displacement-funnel; the solution evaporated to dryness; the granular residue suspended in water and pressed in a linen cloth; and the remaining substance is once boiled up with a sevenfold quantity of water, and quickly filtered into a bottle, which must be completely filled with, it and set aside: the catechin which separates after a day is collected on linen, pressed and dried. (Fr. Nees v. Esenbeck, Guibourt.) The aqueous solution of the ethereal extract also yields catechin when evaporated in vacuo; and the mother-liquor does not yield any more of that substance on exposure to the air. (Neubauer.) — 2. When 1 pt. of finely powdered catechu is macerated for 24 hours with 3 pts. of cold water, and the brownish grey residue is boiled with 8 pts. of water, the brown filtrate deposits in a few hours a large quantity of granular, brownish, impure catechin. The residue, if repeatedly boiled with water, yields an additional quantity and less coloured. After washing with cold water, the product becomes still whiter and dries up to a brittle pearly mass, which, when dissolved in 6 pts. of boiling water and digested with purified animal charcoal, separates from the filtrate perfectly white, and remains white after washing with cold water and drying in vacuo over oil of vitriol. When dried in the air, it turns yellowish. — When alkaline animal charcoal — that, for example, which is obtained in the preparation of ferrocyanide of potassium — is used, a brown solution is obtained, which may indeed be decolorised by hydrochloric acid, but does not yield crystalline catechin till it is evaporated, and then only in small quantity. — Büchner's statement that Bengal catechu yields more catechin than other varieties, is incorrect. (Wackenroder.)—3. Büchner macerates 8 pts. of finely pulverised Bengal or Bombay catechu with 32 pts. of cold water for a week, leaves it to settle for four or five days, then decants, and repeats this treatment three or four times, but always with a double quantity of water. The residue is dissolved in an eight-fold quantity of boiling water; and the solution, in order to precipitate colouring matter, is gradually mixed with a hot solution of basic acetate of lead, till a filtered sample exhibits only a wine-yellow colour, and then very quickly filtered. The white granular precipitate which separates on cooling is dissolved in boiling water; the solution clarified with white of egg and poured into a bottle which can be closed; the liquid decanted; the separated catechin heated with water till it dissolves; the solution left to cool slowly; and the catechin which then separates, collected on

a filter, washed and dried. — As thus obtained, it is still impure. It is therefore dissolved in warm water and completely precipitated by neutral acetate of lead; the lead-compound decomposed by sulphuretted hydrogen; the sulphide of lead (which retains the impurities), exhausted with a large quantity of water, at 90°; and the catechin which crystallises on cooling, is pressed as quickly as possible between bibulous paper and dried in vacuo over oil of vitriol. (Svanberg, Hagen.) Neubauer adopts a similar method, omitting however the partial decoloration with basic acetate of lead. — 4. Finely pulverised catechu is washed with cold water on a filter by displacement till the water runs through colourless; it is then quickly dried between paper, and digested with warm alcohol, so long as white specks of the acid make their appearance as the residue is dried. The alcohol is then distilled to one-half; the resulting brown precipitate collected on a filter; the filtrate evaporated to one-half at 40°, and then left to cool; the greyish brown catechin which separates after some hours, dried between paper and dissolved in warm water; the solution mixed with a sufficient quantity of basic acetate of lead to render it colourless; the dissolved lead-salt decomposed by sulphuretted hydrogen; and the solution boiled and filtered: it then deposits colourless catechin on cooling. (Dahlström.) Winckler removes the dissolved lead-salt by means of sulphate of soda and filters the liquid from the sulphate of lead while still hot. Zwenger evaporates the alcoholic solution to one-third of its bulk (without distilling, because the mass jumps violently); presses between linen the yellowish brown paste which is obtained on cooling; dissolves the residue in boiling water; filters; redissolves the slightly coloured acid which separates on cooling, in boiling water; precipitates the solution, while still hot, with neutral acetate of lead; and treats the precipitate as in Svanberg's process (3).

5. The catechin which separates from an aqueous solution of catechutannic acid exposed to the air, is pressed between paper and recrystallised from hot water. (Delffs.) — In a tan-pit in which a particularly red catechu was used, Th. Cooper found the leather covered with a whitish crust which was regarded as a sign that the tanning was complete. When this deposit was washed with cold water, dissolved in a treble quantity of boiling water, and filtered hot, the filtrate on cooling yielded catechin. — [According to Neubauer, catechin is not formed by oxidation of catechutannic acid (vid. *sup.*)].

The filters through which a solution of catechin is to be passed, must be previously washed with hydrochloric acid, because the catechin would be coloured by the presence of iron or of alkalis.

Hydrated catechin obtained as above is rendered anhydrous by fusion.

| | | | Zwenger. | Svanberg. |
|---|---|---|---|---|
| 14 C | 84 | 60·87 | 61·36 | 61·66 |
| 6 H | 6 | 4·35 | 4·83 | 4·72 |
| 6 O | 48 | 34·78 | 33·81 | 33·62 |
| $C^{14}H^{6}O^{6}$ | 138 | 100·00 | 100·00 | 100·00 |

Isomeric with salicylic and oxybenzoic acids.

*Decompositions.* 1. Catechin heated above its melting point, swells up strongly, gives off inflammable vapours having a peculiar penetrating odour like that of burnt horn, and leaves a shining very combustible charcoal. When subjected to dry distillation, it gives off carbonic acid

and carbonic oxide, and water passes over containing pyrocatechin and a volatile oil. (Wackenroder, Zwenger) — Exposed to the air in the moist state, it takes up oxygen and gradually turns brown, with peculiar quickness in contact with alkalis, and then precipitates a solution of gelatin. The colourless saturated aqueous solution acquires a lemon-yellow colour by a few hours' exposure to the air. (Wackenroder.) When a mixture of catechin and water is heated in contact with the air, a dark red liquid is formed, which when evaporated, leaves a red gelatinous mass, easily soluble in water (Svanberg); the solution precipitates gelatin (Esenbeck), and according to Guibourt, contains a substance intermediate between catechin and rubic acid. Catechin exposed to the air in contact with potash or ammonia takes up oxygen and becomes, first rose-coloured, then bright red, then dark red, and ultimately black, japonic acid being produced; this transformation is accelerated by heating with excess of alkali.—¶. According to Neubauer, catechin is converted by exposure to the air into catechutannic acid. When the ethereal extract of Bombay catechu was repeatedly crystallised from water, there remained, after the first crystallisation, a reddish brown mother-liquor which precipitated a solution of gelatin and appeared therefore to contain catechutannic acid; the mother-liquors of the following crystallisations were yellowish, but on exposure to the air and especially if evaporated, assumed a reddish colour, and acquired increased power of precipitating a solution of gelatin. On further evaporating the entire liquid, it assumed a deep brown colour, like an aqueous extract of Bombay catechu, and when evaported to dryness, left a residue exactly resembling the original catechu. A solution of perfectly pure catechin, which does not precipitate gelatin, acquires that power by boiling for several hours; it is difficult however to render the transformation quite complete. (Neubauer.) ¶. — The solution of catechin in cold alkaline carbonates becomes red when exposed to the air, a rubate of the alkali being formed; if the liquid be heated, japonic acid is produced at the same time. (Svanberg, Zwenger, Cooper.) — 3. Catechin dissolves gradually in moderately strong nitric acid, giving off red fumes, and forms a yellow liquid containing oxalic acid. (Esenbeck, Wackenroder, Zwenger.) — 4. Catechin dissolves in oil of vitriol, with partial decomposition, forming a yellow-brown liquid. (Esenbeck, Zwenger.) The solution when heated, assumes a purple colour and ultimately becomes black. (Wackenroder.) ¶ When catechin is boiled with dilute sulphuric acid (1 pt. oil of vitriol to 24 pts. water) a cinnamon-coloured body separates, which, when dried in the air at the ordinary temperature, contains $C^{17}H^{10}O^{10}$ + 3Aq and gives off 3 At. water at 100°. [The substance dried at 100° yielded 53·17 p. c. C and 5·45 H (calc. 53·13 C and 5·21 H), and the quantity of water given off at 100° was 14·4 p. c., the calculated quantity for 3 At. being 14·0 p. c.] The solution filtered from this cinnamon-coloured substance, after being freed from sulphuric acid by means of carbonate of baryta and from undecomposed catechin by repeated precipitation with acetate of lead, does not contain sugar or any substance capable of reducing a solution of oxide of copper. Catechutannic acid boiled with dilute sulphuric acid also yields a brown substance apparently identical with that just mentioned. (Neubauer.) ¶ — 5. The aqueous solution of catechin treated with chlorine, first assumes a wine-yellow colour, then decomposes and becomes colourless. (Wackenroder.) — 6. It gradually reduces the solutions of the noble metals, or immediately if heat be applied.

*Combinations.* With water. *a. Hydrated Catechin.* For the preparation see page 388.

*Properties.* White light laminar mass, having a faint silky lustre; crystallises from a hot-saturated solution by slow cooling in slender needles acuminated at the ends, and often united in tufts. Melts at a gentle heat; at 217°. (Zwenger.) Has a purely astrigent taste, with sweetish aftertaste (Esenbeck); tasteless (Wackenroder); bitter and slightly astringent (Zwenger); sweetish (Büchner). Reddens litmus slightly. (Esenbeck, Dahlström, Wackenroder.) Neutral to litmus. (Döbereiner, Zwenger.) After drying in vacuo, it contains 3 At. water; in vacuo over oil of vitriol, 2 At.; and at 100°, 1 At. which escapes when the substance is melted.

| | *At* 100°. | | Zwenger. | Hagen. |
|---|---|---|---|---|
| 14 C | 84 | 57·14 | 58·64 | 56·85 |
| 7 H | 7 | 4·76 | 5·06 | 5·20 |
| 7 O | 56 | 38·10 | 36·30 | 37·95 |
| $C^{14}H^{8}O^{6}$ + Aq | 147 | 100·00 | 100·00 | 100·00 |

The excess of hydrogen and oxygen in Zwenger's analysis of catechin dried at 100°, over the quantity of hydrogen and oxygen in anhydrous catechin, is to the total quantity as 1 : 8·8. (L.)

| | *In vacuo over oil of vitriol.* | | Delffs. |
|---|---|---|---|
| 14 C | 84 | 53·85 | 54·23 |
| 8 H | 8 | 5·13 | 5·43 |
| 8 O | 64 | 41·02 | 40·34 |
| $C^{14}H^{8}O^{6}$ + 2Aq | 156 | 100·00 | 100·00 |

| | *In vacuo.* | | Hagen. |
|---|---|---|---|
| 14 C | 84 | 50·91 | 50·90 |
| 9 H | 9 | 5·45 | 5·58 |
| 9 O | 72 | 43·64 | 43·52 |
| $C^{14}H^{8}O^{6}$ + 3Aq | 165 | 100·00 | 100·00 |

¶. According to Neubauer, catechin dried at 100° is anhydrous and has the composition $C^{17}H^{9}O^{7}$; and, the air-dried compound contains 3 At. water, the quantity given off at 100° being 14·34 p. c. (by calculation, 13·92.)

| | *At* 100°. | | Neubauer. *a.* | *b.* | *c.* | *d.* |
|---|---|---|---|---|---|---|
| 17 C | 102 | 61·08 | 61·14 | 61·20 | 61·37 | 61·18 |
| 9 H | 9 | 5·39 | 5·27 | 5·17 | 5·51 | 5·10 |
| 7 O | 56 | 33·53 | 33·59 | 33·63 | 33·12 | 33·72 |
| $C^{17}H^{9}O^{7}$ | 167 | 100·00 | 100·00 | 100·00 | 100·00 | 100·00 |

*a* and *b* were prepared from Bombay catechu; *a* by extraction with ether (method 1, page 388); *b* by extraction with boiling water from the residue left after digestion with cold water (method 3, p. 388); *c* and *d* were prepared from Gambir catechu, *c* by extraction with ether, *d* by extraction with water, &c., according to Wackenroder's method (2, p. 388). The numbers in *a* are calculated from the analysis of the hydrated compound (*infra*). A direct analysis of the same preparation which had become yellow by continued drying at 100°, yielded 62·62 per cent. C and 5·24 H, indicating decomposition. Neubauer's analyses of the compound dried at 100°, agree very nearly with Svanberg's and Zwenger's analyses of the melted catechin (*vid. sup.*).

| | Air-dried. | | | Neubauer. a. | Neubauer. b. |
|---|---|---|---|---|---|
| 17 C | 102 | | 52·58 | 52·62 | 52·52 |
| 12 H | 12 | | 6·18 | 6·09 | 6·12 |
| 10 O | 80 | | 41·24 | 41·29 | 41·36 |
| $C^{17}H^{12}O^{10}$ | 194 | | 100·00 | 100·00 | 100·00 |

*a* from Bombay catechu by extraction with ether; *b*, from Gambir catechu also with ether. ¶.

*b. Aqueous Catechin.* Hydrated catechin dissolves in 16000 pts. of water at 5° (Büchner), in 1133 pts. at 17° (Wackenroder), and in 3 or 4 pts. of boiling water (Büchner, Wackenroder); the hot saturated solution solidifies on cooling in consequence of the separation of crystalline needles. — Dry catechin mixed with 2 pts. of cold water swells up and forms a thick pulp which at 80° forms a clear solution. (Wackenroder.)

Catechin dissolves without decomposition in dilute sulphuric and in heated hydrochloric acid.

In the dry state it absorbs ammoniacal gas, but gives it off completely when heated or in vacuo. (Svanberg, Zwenger.) In aqueous solutions of ammonia or the fixed alkalis, it dissolves without decomposition at first, forming a colourless liquid.

In baryta-water, lime-water, or in acetate of baryta or lime, it does not form any precipitate, even on addition of ammonia. (Wackenroder, Zwenger.) It forms with acetate of baryta a white precipitate insoluble in water, which gradually turns brown on exposure to the air. (Svanberg.)

With bichromate of potash, it forms a yellow-brown precipitate which, according to Wackenroder, is not soluble either in potash or in hydrochloric acid, but according to Delffs, dissolves in hydrochloric acid.

*Catechin with Lead-oxide.* — *a.* Aqueous catechin forms with basic acetate of lead, a precipitate which, after being washed with water, loses its white colour, even when dried in vacuo. (Hagen.)

| | | | Hagen. |
|---|---|---|---|
| 2 PbO | 223·6 | 60·34 | 62·07 |
| 14 C | 84·0 | 22·66 | 22·04 |
| 7 H | 7·0 | 1 89 | 1·83 |
| 7 O | 56·0 | 15·11 | 14·06 |
| $C^{14}H^{6}O^{6}$,2PbO + HO | 370·6 | 100·00 | 100·00 |

*b.* Aqueous catechin forms with neutral acetate of lead, an abundant white precipitate which afterwards turns reddish (Esenbeck), dissolves gradually during washing and turns yellow in contact with the air; hence it must be quickly pressed and dried in vacuo over oil of vitriol. (Svanberg.)

| | | | Svanberg. |
|---|---|---|---|
| PbO | 111·8 | 44·75 | 45·16 |
| $C^{14}H^{6}O^{6}$ | 138·0 | 55·25 | |
| $C^{14}H^{6}O^{6}$,PbO | 249·8 | 100·00 | |

¶. Neubauer, by treating a moderately warm solution of catechin with neutral acetate of lead, obtained a nearly white precipitate which, after being washed and dried as quickly as possible, was found to contain:

| | *At* 100°. | | Neubauer. |
|---|---|---|---|
| 2 PbO | 223·6 | 57·24 | 57·44 |
| 17 C | 102·0 | 26·15 | 26·26 |
| 9 H | 9·0 | 2·30 | 1·97 |
| 7 O | 56·0 | 14·31 | 14·33 |
| $C^{17}H^{9}O^{7},2PbO$ | 390·6 | 100·00 | 100·00 |

The compound is very unstable, becoming brown when dried. ¶.

A weak alcoholic solution of catechin forms with *ferrous sulphate* a beautiful green liquid, without precipitation (Esenbeck); at first there is no action; but afterwards the liquid assumes a green colour and deposits a black precipitate; on adding acetate of soda, the colourless mixture immediately assumes a violet-blue colour, and yields a blue-black precipitate very soluble in acetic acid; an alkaline solution of catechin immediately forms with ferrous sulphate a violet-black precipitate. (Wackenroder, Zwenger.) With solutions of *ferric oxide* it forms a copious green precipitate, changing to brown; ferric hydrochlorate in excess acquires at first a dark green colour, but becomes colourless immediately afterwards and yields a brown precipitate; if the catechin is in excess, the mixture assumes an intense green colour, but afterwards becomes colourless from reduction of the ferric oxide, and sometimes exhibits a greyish green turbidity. (Wackenroder, Zwenger.) — *Cupric* acetate turns brown when mixed with catechin, but does not yield a precipitate; on adding ammonia, a dark brown precipitate is immediately formed. A warm solution of catechin immediately forms a precipitate which soon turns black. (Svanberg, Zwenger.) The alkaline solution added to excess of solution of cupric sulphate, produces a fine green colour, and after some time a cinnabar-coloured precipitate; if the catechin is in excess, this precipitate is formed immediately. (Wackenroder.) — With *mercurous* nitrate, it forms a copious white precipitate which afterwards turns grey from reduction; with *mercuric* nitrate, a dingy white precipitate which afterwards turns reddish. (Esenbeck.) The precipitate formed with a mercuric salt dissolves in acetic acid, and on adding hydrochloric acid to the solution, a precipitate of calomel is formed. In a solution of corrosive sublimate, a precipitate is formed which dissolves in acetic acid or in common salt. (Wackenroder.) — Nitrate of *silver* is not precipitated by solution of catechin; but on heating or on addition of ammonia, a black precipitate is immediately formed, which does not dissolve in nitric acid or in ammonia. (Svanberg.) — *Chloride of gold* or solution of chloride of gold and potassium forms with catechin a red-brown precipitate, which dissolves with yellow colour in a large quantity of water. The hot solution reduces the gold. (Esenbeck, Svanberg.) Chloride of *platinum* and sodium forms with catechin a yellow liquid which when heated, slowly deposits metallic platinum. (Svanberg.)

Catechin dissolves readily in *alcohol* and *ether;* in 2 or 3 pts. of boiling alcohol; in 120 pts. of cold alcohol; in 7 or 8 pts. of boiling ether (Büchner); in 5 or 6 pts. of cold alcohol, in 2 or 3 pts. of boiling alcohol,

in 7 or 8 pts. of boiling ether. (Wackenroder.) It dissolves in *acetic acid* but not in oil of turpentine.

Catechin does not precipitate solution of gelatin unless it be mixed with hydrochloric or acetic acid. (Döbereiner.) It does not precipitate the vegetable alkaloids.

*Appendix to Catechin.*

## Rubic Acid. $C^{18}H^{6}O^{10}$.

SVANBERG. *Pogg.* 39, 171; *Pharm. Centr.* 1836, 888.

*Formation.* By the action of the air on a solution of catechin in aqueous alkaline carbonates.

*Preparation.* Catechu is dissolved in aqueous carbonate of potash, and the liquid left to evaporate in the air without application of heat. The residue is finely pulverised and stirred up with water; the solution filtered after a short time; the excess of carbonate of potash carefully decomposed by acetic acid; the liquid filtered as quickly as possible, from any rubic acid that may have been precipitated, and the filtrate mixed with alcohol, which separates rubate of potash. This salt is washed with alcohol, dissolved in water and mixed with hydrochloric acid; and the precipitate is quickly washed with water, and dried first in vacuo over oil of vitriol, afterwards in the drying apparatus.

Changes into japonic acid even during the washing and drying in vacuo.

Rubate of potash forms with the salts of the earths and heavy metallic oxides, red precipitates which dissolve partially when washed with water.

| *Rubate of Silver.* | | | Svanberg. |
|---|---|---|---|
| 18 C | 108 | 35·88 | 36·04 |
| 5 H | 5 | 1·69 | 2·12 |
| Ag | 108 | 35·88 | 35·47 |
| 10 O | 80 | 26·55 | 26·37 |
| $C^{18}H^{5}AgO^{10}$ | 301 | 100·00 | 100·00 |

## Japonic Acid. $C^{24}H^{8}O^{10}$.

SVANBERG. *Pogg.* 39, 168; *Pharm. Centr.* 1836, 886.

*Formation.* By the action of the air on a solution of catechin in caustic potash.

*Preparation.* A solution of catechin in caustic potash which has turned black by exposure to the air, is supersaturated with acetic acid, and

evaporated nearly to dryness, and the residue is treated with alcohol, which dissolves acetate of potash and leaves acid japonate of potash. This salt is washed several times with alcohol, dissolved in water and mixed with a slight excess of hydrochloric acid, whereby the japonic acid is precipitated, and only a small quantity remains in solution, more however as the excess of hydrochloric acid is greater.

*Properties.* Black. When recently prepared, it dissolves in warm water and is afterwards deposited in black grains. The solution reddens litmus.

| | | | Svanberg. |
|---|---|---|---|
| 24 C | 144 | 62·07 | 61·34 |
| 8 H | 8 | 3·45 | 4·22 |
| 10 O | 80 | 34·48 | 34·44 |
| $C^{24}H^{8}O^{10}$ | 232 | 100·00 | 100·00 |

Japonate of potash evaporated to dryness with excess of acetic acid, is converted into an acid salt. With the hydrochlorates of baryta, lime, alumina, glucina and yttria, it forms bulky precipitates insoluble in cold dilute nitric acid. With sulphate of copper, it forms a dark green precipitate.

*Japonate of Silver. a. Acid.*

| | | | Svanberg. |
|---|---|---|---|
| 24 C | 144 | 42·48 | 48·23 |
| 7 H | 7 | 2·06 | 2·47 |
| Ag | 108 | 31·86 | 32·24 |
| 10 O | 80 | 23·60 | |
| $C^{24}H^{7}AgO^{10}$ | 339 | 100·00 | |

*b. Neutral.* By precipitating nitrate of silver with neutral japonate of potash. Black precipitate, which is decomposed by potash, but not by hydrochloric acid.

| | | | Svanberg. |
|---|---|---|---|
| $C^{24}H^{6}O^{10}$ | 230 | 51·57 | |
| 2 Ag | 216 | 48·43 | 48·22 |
| $C^{24}H^{6}Ag^{2}O^{10}$ | 446 | 100·00 | |

Japonic acid is insoluble in alcohol.

## Gallic Acid.

$C^{14}H^{6}O^{10} = C^{14}H^{6}O^{4},O^{6}$ or $C^{14}H^{6}O^{2},O^{8}$.

SCHEELE. (1785.) *Opusc.* 2, 224.
RICHTER. *N. Gegenstände d. Chemie.* 1, 62; 11, 67.
TROMMSDORFF. *A. Tr.* 8, 105.—*N. Tr.* 2, 142.
DAVY. *Journal of the Royal Institution,* 15, 273; *A. Gehl.* 1, 567.
BOUILLON LAGRANGE. *Ann. Chim.* 60, 156; *N. Gehl.* 3, 623.
DÖRFFURT, BERTHOLLET, PROUST, FERNANDEZ & BOUILLON LAGRANGE. *A. Gehl.* 6, 220.
PFAFF. *N. Gehl.* 5, 327.
SENTÜRNER. *Schw.* 4, 410.
BERZELIUS. *Ann. Chim.* 94, 303.
BRACONNOT. *Ann. Chim. Phys.* 9, 181; *N. Tr.* 3, 2, 393.
CHEVREUL. *Mem. du. Mus.* 1828. Cah. 11, 374.
BROOKE. *Phil. Ann.* 6, 119.
DÖBEREINER. *Schw.* 61, 380; *Pharm. Centr.* 1831, 204.
WACKENRODER. *N. Br. Arch.* 28, 14 — *J. pr. Chem.* 23, 209. — *Ann. Pharm.* 31, 73. — *Pharm. Centr.* 1841, 477; 1842, 3.—*J. pr. Chem.* 24, 33.
PELOUZE. *Ann. Chim. Phys.* 54, 337; *Pharm. Centr.* 1834, 336.
LIEBIG. *Ann. Pharm.* 10, 176; *Pharm. Centr.* 1854, 746.—*Ann. Pharm.* 26, 126 and 162; *Pharm. Centr.* 1838, 530.
ROBIQUET. *J. Pharm.* 22, 487; *J. pr. Chem.* 81, 125; *Repert.* 59, 56; *Pharm. Centr.* 1836, 634. — *Ann. Chim. Phys.* 64, 385 and 396; *Pharm. Centr.* 1837, 514.
HARFF. *N. Br. Arch.* 5, 291; *Pharm. Centr.* 1836, 324.
BLEY. *N. Br. Arch.* 26, 169; *Pharm. Centr.* 1841, 619.
LAROCQUE. *J. Pharm.* 27, 197; *J. pr. Chem.* 24, 34; *Ann. Pharm.* 39. 97; *Pharm. Centr.* 1841, 716.
BARRESWILL. *Compt. rend.* 17, 739; *J. pr. Chem.* 30, 379.
STENHOUSE. *Phil. Mag. J.* 22, 419; *Pharm. Centr.* 1843, 225.
PH. BÜCHNER. *Ann. Pharm.* 53, 175 and 349.
WETHERILL. *N. J. Pharm.* 12, 107; *J. pr. Chem.* 42, 247; *Pharm. Centr.* 1847, 749.
A. STRECKER. *Ann. Pharm.* 90, 328; *J. pr. Chem.* 62, 434.
W. KNOPP. *Pharm. Centr.* 1854, 860; 1855, 657, 737.

*Gallapfelsäure, Gallussäure, Acide gallique.* — First examined by the Dijon academicians, contaminated however with tannic acid. First prepared in the pure state by Scheele.

*Sources.* In gall-nuts (Scheele), in the *Sumach* and *Dibidivi* (Stenhouse); in the gummy exudation of the sumach (Fernandez); in *Cytisus Hypocystis, Flores Arnicæ, Semen Sabadillæ, Radix Hellebori albi* and *nigri, R. Colchici autumnalis, R. Ipecacuanhæ* and *Cortex Angusturæ spurius;* in green and black tea, in the acorns of *Quercus ægylops* (not in oak-bark, catechu or kino), in the shell of the fruit of *Terminalia Chebula,* in *R. Bistortæ,* in the fruit of *Anacardia bryofolia;* in *R. Senegæ,* the leaves of *Coriaria myrtifolia,* the fruit of *Myrtus Pimenta* and *Bertolletia excelsa,* in Sandal-wood, in *Lycopus europ., Linum latifolium,*

*Fol. Uvæ ursi* (Kawalier); in *Rad. Plumbaginis europ.;* in Acaju-nuts (Vicira de Mättos); in the bark of the pomegranate root (A. Latour de Trie), in mango-seeds (Avequin); in the fruit of *Musa paradisiaca* (Boussingault), in rhubarb-root (Brandes); in *Flores Arnicæ*, and *Radix Strychnos Nux vomica;* and probably in most of the astringent parts of plants. (Higgins, *Schw.* 5, 46.)

*Formation.* From *Quercitannic Acid.* 1. By boiling with potash-ley or dilute sulphuric or hydrochloric acid (Liebig), with simultaneous formation of a hydrate of carbon (Liebig), of glucose (Stass. *Ann. Pharm.* 30, 205; Strecker):

$$2C^{54}H^{22}O^{34} + 16HO = 6C^{14}H^{6}O^{10} + C^{24}H^{24}O^{24};$$

(compare Knop, *Pharm. Centr.* 1855, 748.) — 2. By fermentation. (vid. Tannic acid.)

*Preparation.* 1. An aqueous infusion of gall-nuts is evaporated to dryness; the pulverised residue exhausted with absolute alcohol; the liquid filtered; the greater part of the alcohol removed from the yellowish filtrate; the residue diluted with water; and the liquid evaporated to the crystallising point. (Richter.) — This process yields but a small quantity of gallic acid, and according to Pfaff, contaminated with tannic acid. — Infusion of gall-nuts is mixed with acetic acid to decompose the gallate of lime, and then shaken up with ether. There are then formed three layers, the uppermost containing gallic acid, which may be crystallised by evaporation. (Döbereiner.)

2. An aqueous extract of *sumach* is precipitated with gelatin; the filtrate evaporated; the residue exhausted with alcohol; the alcohol distilled off; and the residue digested with ether. The ethereal solution yields an abundant crystallisation of gallic acid which may be rendered colourless by recrystallisation and treatment with animal charcoal. (Stenhouse.) — An alcoholic infusion of gall-nuts is precipitated with solution of isinglass or white of egg, and digested for a quarter of an hour; the alcohol removed from the filtrate by distillation; and the residual liquid is boiled with charcoal dust, filtered, clarified with white of egg, and slowly evaporated; the gallic acid then crystallises from the brown viscid mother-liquor. (Dörffurt.) — According to Trommsdorff, the acid thus obtained is contaminated with extractive matter. — Barruel & Thénard precipitate infusion of gall-nuts with white of egg, filter, evaporate to dryness, dissolve the residue in water, filter again, and leave the solution to crystallise by evaporation. — The product is small, because, as shown by Berthollet (*A. Gehl.* 6, 226), the precipitate formed by white of egg likewise contains gallic acid, whilst a small quantity of that acid remains in the liquid, and its crystallisation is very much impeded by the presence of albumen. — Braconnot did not obtain any crystallised acid by this process, but an inconsiderable brown residue; chiefly consisting of the salts contained in the large quantity of albumen used in the process. — Gaultier de Claubry (*Ann. Chim. Phys.* 10, 235,) states that he obtained a large quantity of gallic acid by precipitating the infusion with bone-gelatin, evaporating the liquid, and exhausting the residue with alcohol. — Infusion of galls is mixed with carbonate of potash, whereupon tannin is precipitated in combination with carbonate

of potash; the filtrate is precipitated with acetate of lead; and the washed precipitate is decomposed with sulphuric acid. (Richter, Sertürner.) — [These methods are adapted for the detection, but not for the preparation of gallic acid. J. L.]

Davy boils the infusion of galls with carbonate of baryta; filters the bluish-green solution of gallate of baryta from the insoluble compound of baryta with tannic acid and extractive matter; precipitates the baryta by sulphuric acid; filters; evaporates; dissolves the residue in alcohol, which leaves gum undissolved; and again evaporates to the crystallising point. — Fiedler (*A. Tr.* 9, 1, 52) digests infusion of galls with hydrate of alumina, which he supposes to take up the tannic acid and leave the gallic acid in the liquid to be evaporated. But, according to Davy and Pfaff, a large quantity of alumina likewise precipitates the gallic acid; and if by chance a portion of the acid remains in solution, in consequence of the quantity of alumina not being sufficient to precipitate it completely, this portion of acid (according to Davy) contains alumina. — Proust precipitates infusion of galls with solution of protochloride of tin, removes the tin from the filtrate by sulphuretted hydrogen, and evaporates. This process, according to Trommsdorff, yields only $\frac{1}{116}$ of gallic acid, because the free hydrochloric acid exerts a decomposing action, and also because a large portion of the gallic acid is precipitated together with the protoxide of tin.

3. Pure quercitannic acid precipitated by sulphuric or hydrochloric acid is digested for a day with a mixture of 1 pt. oil of vitriol or strong hydrochloric acid and 8 pts. water, the water being renewed as it evaporates, and the liquid is evaporated at a gentle heat to the crystallising point. If strong acid be used and the liquid boiled, the gallic acid obtained is small in quanity, and dark-coloured. The crystals have but little colour and are easily purified. (Stenhouse.) — Liebig precipitates the solution of quercitannic acid with sulphuric acid; adds the precipitate, after it has been washed with dilute sulphuric acid and pressed, to a boiling mixture of 1 pt. oil of vitriol and 2 pts. water as long as it dissolves completely; and boils the liquid for a few minutes. On cooling, it deposits strongly coloured gallic acid, which must be several times recrystallised and then precipitated from the boiling aqueous solution by neutral acetate of lead. The washed precipitate is suspended in water and decomposed by sulphuretted hydrogen, the sulphide of lead exerting a decomposing action. Wetherill boils 50 grms. of dry tannic acid with 500 cubic centimetres of a mixture of sulphuric acid of sp. gr. 1·84 with four times its bulk of water, till the liquid crystallises on cooling; by this process 100 grms. of tannic acid yield 84 grms. of gallic acid.

4. Tannic acid or infusion of galls is added to an excess of boiling dilute potash-ley and boiled for 20 seconds; the solution decomposed by dilute sulphuric acid and once boiled up; and the crystalline magma of sulphate of potash and gallic acid is pressed between paper and well boiled with alcohol: the gallic acid then crystallises on cooling. (Liebig.) — Coarsely pounded gall-nuts freed from the finest powder, are exhausted with water; the infusion evaporated to an extract; and this extract added by small portions to boiling soda-ley of sp. gr. 1·4 till the frothing ceases; the strongly coloured liquid, after being left to cool for a while, is supersaturated with acetic acid; the brown crystalline precipitate is repeatedly washed with cold water and dissolved in boiling water; and the solution is treated with animal charcoal and filtered. The acid which

separates on cooling, has only a brown colour after several recrystallisations, and cannot be decolorised by animal charcoal; but on dissolving it in alcohol, there remains a brown residue, and the solution yields by evaporation, nearly colourless crystals, which may be purified by recrystallisation. By this process, 10 lbs. of gall-nuts yield 12 oz. of pure gallic acid. (Büchner.) Liebig and Link dissolve the gallic acid obtained by treatment with potash-ley and precipitation with acetic acid, in water containing just sufficient hydrochloric acid to remove all the potash, and crystallise it repeatedly till it burns without residue on platinum-foil. In this manner, 100 pts. of quercitannic acid yield from 56 to 60 pts. of gallic acid.

5. One-pt. of pounded galls is digested with 3 pts. of cold water, and the filtered liquid is exposed to the air in open vessels set in a warm place; it then becomes covered with a film of mould which must be frequently removed. After being evaporated to one-half, the liquid is decanted from the crystalline sediment, left to turn mouldy again, &c. The sediments consisting of impure gallic acid are washed with a small quantity of cold water, then dissolved in hot water, filtered and crystallised. (Scheele.) [This method yields the largest product. J. L.]—Trommsdorff boils the sediment together with the mould with alcohol instead of water, filters, adds water, and distils off part of the alcohol; white gallic acid is then deposited as the liquid cools, and brownish acid on evaporating the mother-liquor, the total product amounting to $\frac{1}{7}$ of the weight of the galls. — According to Braconnot, the infusion of galls is set aside for some months in open bottles, the mouldy crust removed, the crystals separated from the liquid by pressure between linen, and the liquid evaporated to a syrup: it then deposits an additional quantity of gallic acid. Powder of galls which has been exhausted with boiling water, when left to itself in the moist state for two months, and then extracted with hot water, likewise yields a small quantity of gallic acid. 20 lbs. of galls thus treated yield 5 pts. of impure acid, and when this impure acid is dissolved in boiling water, treated with purified animal charcoal, filtered (ellagic acid then remaining on the filter), cooled, and the remaining mother-liquor further evaporated and cooled, 4 pts. of the pure acid are obtained. — According to Braconnot, also, entire gall-nuts continually moistened with water during a month in summer, swell up, become covered with mould, and are reduced to a whitish pulp, and when this pulp is freed from a brownish liquid by pressure between linen, boiling water likewise extracts gallic acid from it. A similar method may be adopted with powder of galls. — Büchner obtained by Braconnot's process, a yellowish white powder, which when treated with hot water, yielded a turbid liquid running turbid through the filter, but dissolved in boiling alcohol, with the exception of a residue probably consisting of ellagic acid, and separated therefrom in pure crystals, amounting to $1\frac{1}{2}$ lb. from 10 lbs. of galls. (Compare further, Martius, *Pharm. Centr.* 1831, 224; Fr. Müller, *N. Br. Arch.*, 46, 152). Wittstein (*Viertelgahrschr. pr. Pharm.* 2, 72) obtained, from Chinese gall-nuts which had been moistened in the powdered state with water and exposed to the air for 6 weeks at a moderate heat, scarcely 17 per cent. of gallic acid; but, after addition of ordinary gall-nuts or beer-yeast, nearly 50 per cent. — Steer (*Wien. Akad. Ber.* 22, 249; *Chem. Gaz.* 1857, 430) stirs up 100 lbs. of the best Turkish gall-nuts pounded as finely as possible to a thin paste with water; leaves the mixture to itself for 10 days, stirring frequently and renewing the water as it is absorbed; decants

the liquid after adding more water; exhausts the residue in a wooden displacement apparatus; decants and strains all the extracts after the deposit has settled; leaves the liquid in large loosely covered pans in a warm place for three or four months till all the gallic acid has separated out; rinses the yellowish red acid thus obtained with distilled water; dries the product (the dried acid thus obtained from 100 lbs. of gall-nuts amounted on the average to 24 lbs.); dissolves it in boiling water; leaves it to settle in a warm place; digests the decanted liquid with purified blood-charcoal; filters through paper free from iron; leaves the filtrate to crystallise; and puts the pure acid immediately into well-closed vessels to protect it from ferruginous dust. — Kent (*Sill. Ann. J.* 24, 314) agitates common ink with ether, decants the ether and distils, and thus obtains a large quantity of gallic acid. The ink, after this treatment, is as good as ever. — Berzelius previously decomposes the gallate of iron in the ink with hydrochloric acid. — The preparation from acaju-nuts is described by Vicira de Mattos. (*J. Pharm.* 17, 625.) From mango-seeds, gallic acid is obtained by extraction with water, boiling with white of egg, and evaporating the filtrate: product, 10 per cent. (Avequin, *J. Pharm.* 17, 432.)

To detect traces of quercitannic acid in gallic acid, Wackenroder (*N. Br. Arch.*) adds sulphate of quinine, which then produces turbidity.

*Properties.* Crystallises from the hot aqueous solution in slender white silky needles (Braconnot); in prisms belonging to the doubly oblique prismatic system. *Fig.* 126 (oP . 'P . ∞'P . ∞P' . ∞P∞); cleavage parallel to *y*, less distinct parallel to *u*; $y : u = 95°$; $y : v = 125° 20'$; $u : v = 84°$; $v : z = 160°$; $y : n = 116°$; $u : a$ about 150°. (Brooke, *Phil. Ann.* 6, 119; compare Wackenroder, *J. pr. Chem.* 23, 209; Guibourt, *Rev. scient.* 3, 36.) Colourlesss. Has a harsh, slightly acid taste and reddens litmus. Bley (*N. Br. Arch.* 36, 169.) Gives off 9·45 p.c. (2 At.) water at 120. (Pelouze.)

| | *At* 120°. | Pelouze. | | Liebig. | Liebig & Otto. | Stenhouse. *a.* | *b.* | *c.* |
|---|---|---|---|---|---|---|---|---|
| 14 C | 84 | 49·41 | 49·49 | 49·18 | 49·37 | 49·25 | 49·31 | 49·22 |
| 6 H | 6 | 3·53 | 3·65 | 3·64 | 3·58 | 3·70 | 3·70 | 3·75 |
| 10 O | 80 | 47·06 | 46·86 | 47·18 | 47·05 | 47·05 | 46·99 | 47·03 |
| $C^{14}H^{8}O^{10}$ | 170 | 100·00 | 100·00 | 100·00 | 100·00 | 100·00 | 100·00 | 100·00 |

The acid analysed by Pelouze and by Liebig was prepared by 5; Stenhouse's acid *a*, from sumach by 2; *b* from sumach by 3; and *c* from dibidivi by 2.

*Decompositions.* The dry acid carefully heated to between 210° and 215°, gives off pure carbonic acid gas, and yields a sublimate of pyrogallic acid, without any other product:*

$$C^{14}H^{6}O^{10} = C^{12}H^{6}O^{6} + 2CO^{2}.$$

it likewise gives off carbonic acid when quickly heated to 250°; in that case, however, no pyrogallic acid sublimes, but water distils over and metagallic acid remains in the retort. (Pelouze.)

$$2C^{14}H^{6}O^{10} = C^{24}H^{5}O^{5} + 4CO^{2} + 4HO.$$

* Water and metagallic acid are always formed at the same time [J. L.].

Between 225° and 236°, the acid melts and boils, and, after three hours, yields a red-brown mass with a blackish lustre, which dissolves almost completely in cold water, and precipitates a solution of gelatine, but not the vegetable bases (the *gallhumic acid* of Berzelius). At a still higher temperature, the residue consists chiefly of metagallic acid, insoluble in water, but soluble in alkalis. The decomposition is not so simple as it is given by Pelouze; water and gallhumic acid are produced at every stage of the distillation. (Robiquet: *comp.* Braconnot, Wackenroder.) [The largest amount of pyrogallic acid is obtained by mixing the gallic acid (34 to 36 p. c.) with 2 pts. of coarsely pounded pumice-stone, and heating in a stream of carbonic acid. J. L.] By rapid distillation there is obtained, in addition to pyrogallic acid, a crystalline granular sublimate of a scarlet or brown-red colour. (Wackenroder.) — 2. Gallic acid burns in the air, leaving a black, combustible charcoal. (Scheele.) — 3. The aqueous solution remains unaltered if excluded from the air; but in contact with the air, it decomposes, with formation of fungi and a black humus-like substance. (Pelouze.) — 4. Gallic acid remains unaltered in contact with alkalis, so long as no oxygen gas comes in contact with it; but in contact with oxygen, it decomposes, the more quickly and strongly as the alkalies are in greater excess, probably because these bodies have but little affinity for gallic acid and rather dispose its constituents to arrange themselves, under the influence of the absorbed oxygen, in the form of other compounds, such as humus, carbonic acid, and perhaps also acetic acid; the peculiar colours produced at the same time are due to the formation of one or more coloured products of decomposition not yet investigated. — The tints thus produced are: with a small quantity of *ammonia:* yellow; with a large quantity, red-brown; with a small quantity of *potash:* green, after a while; with a large quantity: first yellow, then red and brown; with a small quantity of *baryta-water:* reddish yellow; with a large quantity: blue with greenish blue flakes; with a small quantity of *strontia*-water: pale yellow; with a large quantity: greenish blue with blue flakes; with a small quantity of *lime*-water: reddish yellow; with a large quantity: violet-green with flakes of similar colour. (Gm. 4 Aufl. ii. 164.) — Caustic soda acts with aqueous gallic acid in the same way as caustic potash; carbonate of potash acts in a similar manner, but more slowly (Büchner; see also Wackenroder, *N. Br. Arch.* 27, 257.) When Scheele's gallic acid is added to thoroughly boiled lime-water standing over mercury, white flakes are formed, and with a larger quantity of the acid, a pale red solution; oxygen gas passed up to the solution is quickly absorbed, the liquid assuming a greenish blue colour; if hydrochloric acid be then introduced, no carbonic acid is evolved, perhaps on account of the great dilution, but light blue flakes are separated. (Gm.) According to Chevreul (*Dict. des Sc. nat.* 20, 530, and *Mem. du Mus.* 1825, 374,) oxygen gas is absorbed the more quickly and abundantly, the more the alkali is in excess: 0·2 grm. of gallic acid mixed with a small quantity of aqueous potash absorb in a quarter of an hour, 7·5 cub. cent.; in 15 hours, 14·5 cub. cent. of oxygen gas, and produce 10 cub. cent. of carbonic acid gas, which may be expelled by hydrochloric acid. 0·2 grm. of gallic acid mixed with a larger quantity of potash, absorb 19 cub. cent.; if more potash be added, 14·5 cub. cent.; and, on a still further addition of potash, more oxygen is absorbed, in all, 58 cub. centimetres of oxygen gas; similar effects are produced by baryta added in various quantities. When aqueous gallic acid has turned green by the action of a small quantity of alkali and air, it is not coloured red by a larger quantity of

alkali unless it can absorb more oxygen; the green matter is therefore different from the red (which is produced by the action of a larger quantity of oxygen.) Baryta-water neutralised with Scheele's acid is coloured green by oxygen gas; if the baryta be then precipitated by an exactly equivalent quantity of sulphuric acid, the green filtrate yields by evaporation a very acid and harsh-tasting residue, which precipitates gelatin, is free from sulphuric acid, and dissolves in water, alcohol and ether. Hence Chevreul concludes that tannin is formed in this decomposition of gallic acid; but the tannin doubtless existed ready formed in the gallic acid which he used. — According to Döbereiner, 100 pts. of gallic acid absorb 29 pts. of oxygen gas. (*Gilb.* 72, 203. — When a mixture of gallic acid and alkali which has been exposed to the air, is distilled with dilute sulphuric acid, acetic acid passed over. (Bouillon Lagrange.) — 5. Gallic acid mixed with excess of bicarbonate of lime and exposed to the air, forms a bluish liquid which ultimately assumes an indigo colour and forms after some time a small quantity of greenish blue sediment. When gallic acid is heated with excess of bicarbonate of lime, carbonate of lime is precipitated, and the liquid, colourless at first, assumes a dark blue colour, and yields dark blue flakes on addition of alcohol or ether-alcohol. The indigo-coloured solution assumes a fine amethyst-red colour when treated with acids, but becomes blue again on being neutralised with lime. — This product of the decomposition of gallic acid is called by Wackenroder, *gallerythroic acid*, and by Berzelius, *cyanogallic acid*. It is also produced when gallate of baryta turns blue by exposure to the air.

6. Gallic acid is decomposed by *chlorine*. (Proust.) Chlorine-water forms with aqueous gallic acid, a light yellow liquid which after a while becomes brownish yellow, then decomposes completely and becomes colourless. (Wackenroder.) — Gallate of potash is violently attacked by *bromine* and yields a brownish resin. (Cahours, *N. Ann. Chim. Phys.* 19, 507.) — 7. *Nitric acid* heated with gallic acid forms oxalic acid. — 8. It is very quickly oxidised by *iodic acid*. (Millon.) — 9. Aqueous gallic acid mixed with *bichromate of potash* immediately turns brown, and gradually deposits brown flakes insoluble in hydrochloric acid.

10. When it is quickly heated with *oil of vitriol*, pyrogallic acid sublimes, together with a small quantity of yellowish red matter insoluble in water. A mixture of 1 pt. gallic acid and 5 pts. oil of vitriol carefully heated to 140°, becomes first yellow-brown, then rose-coloured, and ultimately dark wine-red; it then contains ellagic and rufigallic acids. (Braconnot, Robiquet.)

11. When gallic acid is boiled down with a solution of 2 pts. chloride of calcium in 5 pts. of water, carbonic acid is continuously given off; and when the liquid attains a temperature of 120° or 122°, a copious yellowish white precipitate is formed consisting of small polyhedral crystals. The precipitate is washed with hydrochloric acid and then with alcohol, pressed between paper and dried at a temperature between 25° and 30°; it tastes like chloride of calcium, with an aftertaste of gallic acid, reddens moist litmus paper, and imparts a permanent black stain to moist paper at the point of contact. After being dried at 30°, it does not give off water at any temperature up to 130°. Immersed in water the crystals become opaque, give up chloride of calcium together with a small quantity of gallic acid, and yield a pulpy mass which, when collected on a filter, exhibits the properties of unaltered gallic acid. The crystals, when carefully heated, yield, first a harsh-tasting

liquid containing a large quantity of hydrochloric acid, and then rose-coloured vapours, which condense to a transparent liquid containing water, hydrochloric acid, and a very changeable red substance, which imparts to cotton a red, or, after impregnation with basic mordants, a violet colour. The residue contains charcoal, and when treated with water, yields a mixture of lime and chloride of calcium. Subjected to dry distillation, it yields pyrogallic acid. (Robiquet.) — When a decoction of gall-nuts is precipitated with chloride of calcium and the precipitate is exposed to the air for several months, it becomes brownish black and deposits a powder, on which shining crystals resembling boracic acid collect. These crystals are permanent in the air; dissolve readily in water and alcohol; melt when heated; then turn brown-black, swell up and take fire, emitting an empyreumatic odour; give off hydrochloric acid when heated with oil of vitriol; and when dissolved in water and mixed with hydrochloric acid, deposit a white powder, which behaves like ellagic acid and forms a yellowish white precipitate with protosulphate of iron. (Hünefeldt, *J. pr. Chem.* 7, 232.)

12. Gallic acid reduces *ferric* salts, and forms with the resulting ferroso-ferric oxide a black-blue compound. (Chevreul, *Pogg.* 17, 174.) When an alcoholic solution of gallic acid is mixed with an alcoholic solution of dry ferric sulphate and heated to between 60° and 70°, the liquid assumes a fine blue colour, and deposits ferrous sulphate together with resinous drops which solidify on cooling. (Persoz, *Compt. rend.* 17, 1064; Büchner.) Gallic acid, or an alkaline gallate, forms with excess of ferric hydrochlorate, first a blue-black precipitate, which immediately redissolves with greenish colour, while the gallic acid is decomposed; if the gallic acid is in excess, the precipitate likewise disappears, and the whole of the ferric chloride is reduced. (Wackenroder.) When gallic acid is slowly dropped into excess of ferric sulphate, no colouring is produced or only a transient blue tint; in a solution of ferric oxide mixed with chlorine, no blue colour is produced even by an excess of gallic acid. When a ferric salt is added to excess of gallic acid, and the mixture is treated with neutral acetate of lead, a blue precipitate is formed, which dissolves in oxalic acid, forming a colourless solution; the solution contains both sesquioxide and protoxide of iron. The blue colour is restored by acetate of soda. (Barreswil, *Compt. rend.* 17, 739.) In a solution of ferric chloride mixed with ferricyanide of potassium, the smallest quantity of gallic acid produces prussian blue. (Wackenroder, *N. Br. Arch.* 27, 269.) — Ferric acetate, or a mixture of ferric hydrochlorate and acetate of soda, forms with the smallest quantity of gallic acid, a blue-black precipitate soluble in a large excess of acetic acid; the liquid remains blue black and transparent. — An alkaline gallate in excess forms with ferric hydrochlorate a blue-black liquid in which common salt or acetate of soda produces a precipitate which dissolves in potash, forming a brown-red solution. — A solution of ferrous sulphate free from ferric salt is not coloured by gallic acid at first; but on exposure to the air, the mixture gradually assumes an azure-blue colour, and after 12 hours, a black-blue precipitate separates, the liquid retaining its blue colour. If the solution of ferrous sulphate is mixed with a small quantity of caustic alkali, alkaline carbonate or bicarbonate of lime, it immediately acquires an azure-blue colour on addition of gallic acid, and afterwards yields a precipitate soluble in acetic acid. — A solution of ferrous sulphate mixed with acetate of soda is immediately coloured

azure-blue by gallic acid, and after a while yields a blue precipitate. (Wackenroder, *Ann. Pharm.* 31, 77.)

13. *Cupric* acetate forms with gallic acid a copious red-brown precipitate which dissolves without colour in hydrochloric acid, and forms with potash a brownish yellow solution which deposits scarlet cuprous oxide. A similar reaction is produced with cupric sulphate. (Wackenroder.)

14. Gallic acid gradually reduces the solutions of the noble metals.

15. A solution of 2 to 5 pts. of gallic acid in 80 pts. of water added to an excess of a mixture of strong ammonia and sulphite of ammonia, acquires a fine red colour, which disappears very quickly, especially if the liquid be heated, but returns as it cools, gradually extending from the surface downwards. If the heating in open vessels be often repeated, with addition of fresh ammonia-salt, and the liquid finally left to evaporate in thin layers at about 30°, the whole of the gallic acid will be decomposed, the only products, besides sulphite of ammonia, being amides of carbonic acid and traces of sulphuric acid. — If solutions containing 1 or 2 pts. of gallic acid to 8 pts. of water are treated in the same manner, taking care not to let them become coloured more than necessary, brown crystals are obtained after two or three weeks, which become colourless by recrystallisation, and appear to consist of gallate of hydrylamine (= $2C^{14}H^{6}O^{10},NH^{5},HO$; vid. *Gallamic acid*). (W. Knop, *Pharm. Centr.* 1855, 709.)

*Combinations.* Gallic acid dissolves in 100 pts. of cold and in 3 pts. of boiling water. (Braconnot.)

It expels carbonic acid from its salts. — The *Gallates* are divided, since gallic acid is tribasic,* into *tribasic* (neutral) $C^{14}H^{3}M^{3}O^{10}$, *bibasic* $C^{14}H^{4}M^{2}O^{10}$, and monobasic salts $C^{14}H^{5}MO^{10}$. Besides these, gallic acid likewise forms salts containing 7, 8 or 10 At. of a base to 42 At. C. — The gallates in the dry state are permanent in the air, but in contact with alkaline liquids, they absorb oxygen from the air and become brown or black. In presence of free acid, this decomposition does not take place.

It is only the gallates of the alkalis that are soluble in water.

*Gallate of Ammonia. a. Acid.* — 1. Dehydrated gallic acid is saturated with dry ammoniacal gas, and the excess of ammonia left to evaporate in vacuo. (Robiquet.)

2. Ammoniacal gas is passed, nearly to saturation, into a saturated solution of gallic acid in absolute alcohol; and the separated salt is washed with absolute alcohol, and dissolved in the smallest possible quantity of boiling water, whence it crystallises on cooling. (Büchner.)

The salt prepared by (1) is a white powder with a slight tinge of greyish yellow. (Liebig.) It separates from the aqueous solution in combination with water of crystallisation. (Robiquet.) — By (2): Slender six-sided prisms. The solution has a strong acid reaction. — It does not give off any thing at 100°. (Büchner).

* In the classification given at page 204, vol. vii, gallic acid is placed, as a bibasic acid, among the compounds belonging to the primary nucleus $C^{14}H^{10}$. But, according to Strecker's numerous analyses of the lead-salt (p. 410), it appears to be really tribasic = $C^{14}H^{6}O^{2},O^{8}$, and should therefore be included in the salene-series [$I_{2}$].

| *By* (1). | | | Liebig & Otto. | *Crystallised.* | | | Büchner. |
|---|---|---|---|---|---|---|---|
| 14 C | 84 | 44·92 | 46·16 | 14 C | 84 | 40·97 | 40·95 |
| N | 14 | 7·49 | | N | 14 | 6·85 | |
| 9 H | 9 | 4·81 | 4·82 | 11 H | 11 | 5·36 | 5·38 |
| 10 O | 80 | 42·78 | | 12 O | 96 | 46·82 | |
| $C^{15}H^{5}(NH^{4})O^{10}$ | 187 | 100·00 | | + 2Aq | 205 | 100·00 | |

When immersed in aqueous ammonia and in contact with the air, it gradually turns red and ultimately brown. Hence it cannot be prepared by saturating hydrated or aqueous gallic acid with ammonia. (Robiquet.) — If the alcohol used in the preparation (2) contains a little water, the liquid saturated with ammonia decomposes in contact with the air just like the aqueous solution. (Büchner.)

*Gallate of Potash.* — 1. When an alcoholic solution of gallic acid is mixed with alcoholic potash, a white precipitate is immediately formed, which at first redissolves in the liquid. If potash be added till the surface of the liquid becomes covered with green veins which do not disappear on stirring, soft white flakes separate out, which may be freed from excess of gallic acid by washing with alcohol and dried at a gentle heat. If the slightest excess of potash be added, the liquid acquires a dark green colour, and the colourless salt at first obtained soon becomes dark green and greasy. — The salt cannot be prepared with aqueous solutions.

2. Quercitannic acid is added by small portions to boiling potash-ley of sp. gr. 1·30, as long as brisk effervescence ensues; the liquid, after boiling for some time is saturated with acetic acid; and the gallate of potash which crystallises on cooling is washed with a small quantity of water, repeatedly boiled with alcohol, and obtained nearly colourless by recrystallisation with addition of animal charcoal. (Büchner.)

White crystalline powder, soft and loose after trituration; the acid obtained by 2, is slightly brownish. By continued exposure to the air it becomes covered with a greenish film, but is not perceptibly decomposed. Does not give off any water at 100°. It dissolves very readily in water with slight brown colour; the solution has a strong acid reaction, and if concentrated, deposits the salt in slightly brownish needles on addition of alcohol. (Büchner.)

| | | | Büchner. (1) | Büchner. (2) |
|---|---|---|---|---|
| 2 KO | 94·4 | 15·61 | 15·29 | 15·46 |
| 42 C | 252·0 | 41·69 | 41·65 | 42 08 |
| 18 H | 18·0 | 2·78 | 3·24 | 3·18 |
| 30 O | 240·0 | 39·92 | 39·82 | 39·28 |
| $2C^{14}H^{5}KO^{10} + C^{14}H^{6}O^{10} + 2Aq$ | 604·4 | 100·00 | 100·00 | 100·00 |

*Gallate of Soda.*—Prepared like the potash-salt. 1. — White granular crystalline powder, easily soluble in water; the solution saturated while hot yields needle-shaped laminæ on cooling. The salt gives off 22·03 p. c. (6 At.) water at 100°. With aqueous alkalis it behaves like the potash salt. (Büchner.)

| | | | Büchner. |
|---|---|---|---|
| NaO | 31 | 16·14 | 16·10 |
| 14 C | 84 | 43·75 | 43·13 |
| 5 H | 5 | 2·60 | 2·90 |
| 9 O | 72 | 37·51 | 37·87 |
| $C^{14}H^{5}NaO^{13}$ | 192 | 100·00 | 100·00 |

*Gallate of Baryta.* — Free gallic acid and gallate of soda do not precipitate baryta-salts. With baryta-water not in excess, or with an ammoniacal solution of chloride of barium, gallic acid forms a copious white precipitate, which quickly turns blue in contact with the air. — When recently precipitated carbonate of baryta is added to a boiling concentrated aqueous solution of gallic acid, as long as effervescence ensues, and the mixture is diluted with a large quantity of water and boiled, the pale yellow filtrate deposits on evaporation, slender needles which increase in quantity till nearly all the water is evaporated. When the liquid separated hot from the crystals is left to cool, no more crystals separate out, and when it is left to evaporate spontaneously, only an efflorescence is produced. The crystals are freed from the mother-liquor, washed with alcohol, and quickly dried. — Slender needles, apparently belonging to the hexagonal system. White with a brownish tinge on the surface. Does not give off any water at 100°, but becomes difficult to dissolve in water. It is insoluble in alcohol.

| | | | Büchner. |
|---|---|---|---|
| BaO | 76·6 | 28·95 | 28·85 |
| 14 C | 84·0 | 31·75 | 31·69 |
| 8 H | 8·0 | 3·02 | 3·32 |
| 12 O | 96·0 | 36·28 | 36·14 |
| $C^{14}BaH^{5}O^{10} + 3Aq$ | 264·6 | 100·00 | 100·00 |

*Gallate of Strontia.* — Gallic acid acts upon strontia-salts in the same manner as on baryta-salts. Gallate of strontia is prepared in the same manner as the baryta-salt, but the solution must be evaporated nearly to dryness. White crystals, more soluble in water than the baryta-salt. The aqueous solution reddens litmus. The salt when heated to 100° does not give off water, but is afterwards difficult to dissolve in water; the solution is violet. Insoluble in alcohol. (Büchner.)

| | | | Büchner. |
|---|---|---|---|
| SrO | 52 | 20·88 | 20·79 |
| 14 C | 84 | 33·73 | 33·51 |
| 9 H | 9 | 3·62 | 3.71 |
| 13 O | 104 | 41·77 | 41·99 |
| $C^{14}H^{5}SrO^{10} + 4Aq$ | 249 | 100·00 | 100·00 |

*Gallate of Lime.* — Alkaline gallates form with chloride of calcium a scanty blue-green precipitate (p. 402). A crystalline salt is obtained by treating aqueous gallic acid with carbonate of lime, as in the preparation of the baryta and strontia salts, excepting that no water is added after the saturation with carbonate of lime. — Thin pale yellow crusts made up of adhering needles. At 100°, the salt does not give off water, but

becomes difficult to dissolve in water. From the aqueous solution, alcohol throws down white flakes which become bluish green by exposure to the air.

| | | | Büchner. |
|---|---|---|---|
| CaO | 28 | 12·97 | 13·09 |
| 14 C | 84 | 38·89 | 38·62 |
| 8 H | 8 | 3·70 | 3·79 |
| 12 O | 96 | 44·44 | 44·50 |
| $C^{14}H^{8}CaO^{10} + 3Aq$ | 216 | 100·00 | 100·00 |

*Gallate of Magnesia.* — *a. Basic.* Calcined magnesia immersed in an aqueous solution of gallic acid abstracts all the acid, so that a solution of ferric oxide afterwards added indicates scarcely a trace of gallic oxide.

*b. Tribasic.* — Magnesia stirred up with water is added to a boiling solution of gallic acid, till the acid reaction is very nearly neutralised, If more magnesia be added than is required for complete neutralisation, the liquid becomes green; it must then be decanted and boiled with a small quantity of gallic acid solution, which takes away the green colour. The filtered liquid is evaporated. and the residue is freed from excess of acid by alcohol. Yellowish or brownish white, heavy, slippery to the touch. (Büchner.)

| | | | Büchner. |
|---|---|---|---|
| 3 MgO | 60 | 23·35 | 23·83 |
| 14 C | 84 | 32·68 | 32·20 |
| 9 H | 9 | 3·50 | 3·48 |
| 13 O | 104 | 40·47 | 40·49 |
| $C^{14}H^{3}Mg^{3}O^{10} + 6Aq$ | 257 | 100·00 | 100·00 |

*c.* Magnesia is added to a boiling solution of gallic acid in such quantity as to leave the liquid still strongly acid. (Büchner.)

| | | | Büchner. |
|---|---|---|---|
| 8 MgO | 160 | 22·03 | 21·90 |
| 42 C | 252 | 34·71 | 34·71 |
| 26 H | 26 | 3·58 | 3·61 |
| 38 O | 288 | 39·68 | 39·78 |
| $2C^{14}H^{3}Mg^{3}O^{10} + C^{14}H^{4}Mg^{2}O^{10} + 16Aq$ | 726 | 100·00 | 100·00 |

*d.* Recently precipitated carbonate of magnesia added to a boiling solution of gallic acid dissolves at first; but when a larger quantity is added, the liquid becomes turbid and deposits a heavy powder having scarcely any crystalline character. If the carbonate of magnesia be added in small portions, as long as effervescence ensues, the liquid then decanted, and the precipitate boiled with aqueous gallic acid, it becomes yellowish white after pressing and drying, and dissolves in hydrochloric acid without giving off carbonic acid. (Büchner.)

| | | | Büchner. |
|---|---|---|---|
| 7 MgO | 140 | 20·49 | 19·61 |
| 42 C | 252 | 36·89 | 35·10 |
| 25 H | 25 | 3·66 | 3·65 |
| 37 O | 266 | 38·96 | 41·64 |
| $C^{14}H^{3}Mg^{3}O^{10} + 2C^{14}H^{4}Mg^{2}O^{10} + 14Aq$ | 683 | 100·00 | 100·00 |

*e. Bibasic.* — 1. When a concentrated solution of acetate of magnesia is gently boiled with a strong aqueous solution of gallic acid, acetic acid is given off, and a white precipitate is formed, larger in quantity as the gallic acid is in greater excess. The precipitate is washed with hot water and dried. — 2. When carbonate of magnesia is added to a boiling aqueous solution of gallic acid in such quantity as to leave the liquid still strongly acid, the liquid filtered and quickly evaporated to dryness, and the excess of acid removed by boiling with alcohol, there remains a small quantity of a white powder which contains 17·63 p. c. MgO, 33·46 C and 3·61 H, and according to Büchner, is bibasic gallate of magnesia with 6 At. water, which however requires 16·26 p. c. MgO, and 4·07 H. White, very fine, light powder.

| | | by (1). | Büchner. |
|---|---|---|---|
| 2 MgO | 40 | 17·54 | 17·96 |
| 14 C | 84 | 36·84 | 36·33 |
| 8 H | 8 | 3·51 | 3·46 |
| 12 O | 96 | 42·11 | 42·25 |
| $C^{14}H^{4}Mg^{2}O^{10}$ + 4Aq | 228 | 100·00 | 100·00 |

Gallic acid precipitates hydrochlorate of *cerous oxide*, on addition of a small quantity of alkali, in the form of a brown mass which continually becomes darker in colour, and dissolves in excess of alkali, forming a greenish dark brown solution (Berzelius.) It likewise precipitates the salts of *yttria* and *glucina*.

*Gallate of Alumina.* When recently precipitated hydrate of alumina is added to a boiling aqueous solution of gallic acid, till the liquid no longer exhibits any acid reaction, the liquid retains only traces of acid and the hydrate is not altered in appearance. — A solution of alum is not precipitated by gallic acid unless acetate of soda is added and the liquid heated; the precipitate is contaminated with a basic salt of alumina. — Acetate of alumina heated with gallic acid to between 40° and 45°, yields a bulky precipitate, and if a sufficient quantity of gallic acid be added, the liquid does not retain any alumina. The precipitate when dry forms a bulky white powder, which when heated for some time to between 160° and 200°, does not exhibit any appreciable diminution of weight, and contains 29·48 p. c. $Al^{2}O^{3}$, 29·95 C, and 3·31 H, agreeing with the formula $5C^{14}H^{6}O^{10},8Al^{2}O^{3}+16HO$. (Büchner.)

When *Chromic* sulphate or chrome-alum is boiled with an alkaline gallate, no precipitate is formed; neither does any combination take place when chromic oxide is added to a boiling aqueous solution of gallic acid.

*Gallate of Manganese.* — Concentrated solutions of gallic acid and acetate of manganese, heated together, immediately yield white heavy granules, which assume a brownish tint during washing, and cannot be obtained colourless in the dry state. (Büchner.)

| | | | Büchner. |
|---|---|---|---|
| 7 MnO | 249·2 | 31·34 | 31·28 |
| 42 C | 252·0 | 31·69 | 31·45 |
| 22 H | 22·0 | 2·76 | 2·86 |
| 34 O | 272·0 | 34·21 | 34·41 |
| $C^{14}H^{3}Mn^{2}O^{10}+2C^{14}H^{4}Mn^{2}O^{10}+11Aq$ | 795·2 | 100·00 | 100·00 |

*Gallate of Antimony.* — Tartar emetic forms with gallic acid, or an alkaline gallate, a white slightly crystalline precipitate. The precipitate obtained with free gallic acid is permanent in the air after washing and drying, insoluble in water, and contains 43·21 p. c. $Sb^2O^3$, 29·64 C and 1·92H; it is therefore $5C^{14}H^6O^{10},4Sb^2O^3+6HO$. (Büchner.) When ignited out of contact with the air, it yields a black pyrophoric mass. (Böttger, *Beitr.* 2. 41.)

*Gallate of Bismuth.* — A solution of *magisterium bismuthi* in a large quantity of acetic and a little nitric acid, forms with excess of gallic acid, a yellowish precipitate, which, when dried at 100°, contains 51·42 p. c. teroxide of bismuth. (The formula $C^{14}H^5O^9,BiO^3 + 7Aq$ requires 51·41 p. c.) (Bley.)

*Gallate of Zinc.* — An alkaline gallate is mixed with the solution of a zinc salt, or free gallic acid is added to an excess of acetate of zinc; and the white bulky precipitate, which becomes more crystalline after a while, is washed and then dried at 100°. Pale grey, insoluble in water and in alcohol. (Büchner.)

| | | | Büchner. |
|---|---|---|---|
| 4 ZnO | 162 | 51·59 | 50·74 |
| 14 C | 84 | 26·75 | 26·25 |
| 4 H | 4 | 1·27 | 1·24 |
| 8 O | 64 | 20·39 | 21·77 |
| $C^{14}H^4Zn^2O^{10},2ZnO$ | 314 | 100·00 | 100·00 |

Aqueous gallic acid digested with recently precipitated hydrated oxide of zinc dissolves but little of that substance; the yellowish green liquid yields on cooling silky needles of a zinc-salt. The mother-liquor contains free gallic acid. (Bley.)

*Stannous Gallate.* — When ammonia is added to a solution of protochloride of tin till a permanent precipitate forms, and the liquid is then mixed with excess of gallic acid, a white finely divided crystalline precipitate is produced, which after drying forms a white light powder, insoluble in water. (It is not produced in an acid solution.) (Büchner.)

| | | | Büchner. |
|---|---|---|---|
| 4 SnO | 268 | 63·81 | 62·10 |
| 14 C | 84 | 20·00 | 19·80 |
| 4 H | 4 | 0·95 | 1·25 |
| 8 O | 64 | 15·24 | 16·85 |
| $C^{14}H^4Sn^2O^{10},2SnO$ | 420 | 100·00 | 100·00 |

Bley, by mixing protochloride of tin with gallate of soda, obtained a precipitate containing 55·51 p c. SnO.

*Gallate of Lead. a. Quadribasic.* — Obtained by dropping aqueous gallic acid into an excess of a boiling solution of neutral acetate of lead. The precipitate, which is white and flocculent at first, but becomes light yellow and crystalline on boiling, is washed by decantation and dried at 120°. (Liebig, Büchner, Strecker.)

| | | | Liebig. | Büchner. | Strecker. |
|---|---|---|---|---|---|
| 4 PbO | 447·2 | 75·74 | 76·09 | 76·45 | 76·03 |
| 14 C | 84·0 | 14·25 | 14·62 | 14·12 | 14·39 |
| 3 H | 3·0 | 0·51 | 0·53 | 0·50 | 0·43 |
| 7 O | 56·0 | 9·50 | 8·76 | 8·93 | 9·15 |
| $C^{14}H^{3}Pb^{3}O^{10}$,PbO | 590·2 | 100·00 | 100·00 | 100·00 | 100·00 |

According to Liebig, it is $C^{14}H^{3}Pb^{4}O^{10}$, which requires 76·90 p. c. oxide of lead.

*b. Bibasic.* — Obtained by adding neutral acetate of lead to an excess of warm aqueous gallic acid. The precipitate, if left in the liquid, gradually changes to a grey shining crystalline powder. (Liebig, Büchner.) Gives off 1 At. water between 100° and 160°. (Liebig, Büchner.) In the fresh state it dissolves readily in strong acetic acid. (Büchner.) When touched with burning bodies, it glows like tinder, and, after carbonisation yields a pyrophorus. (Böttger.)

| | | | Liebig. | Büchner. |
|---|---|---|---|---|
| 2 PbO | 223·6 | 58·13 | 57·96 | 57·75 |
| 14 C | 84·0 | 21·84 | 21·66 | 21·82 |
| 4 H | 5·0 | 1·30 | 1·70 | 1·47 |
| 9 O | 72·0 | 18·73 | 18·68 | 18·96 |
| $C^{14}H^{4}Pb^{2}O^{10}$ + 2Aq | 384·6 | 100·00 | 100·00 | 100·00 |

*Gallate of Iron* (p. 403). The compound of gallic acid with ferroso-ferric oxide is obtained of the finest blue colour by adding gallic acid to a mixture of 9 At. ferrous salt to 2 At. ferric salt. The oxide contained in it is therefore $3FeO, 2Fe^{2}O^{3}$, corresponding to ordinary prussian blue. (Barreswil, *Compt. rend.* 17, 739.)

Gallic acid forms with *cupric oxide* a flesh-coloured precipitate soluble in excess of gallic acid: it dissolves also in carbonate of potash, forming a grass-green solution. (Fr. Müller, *N. Br. Arch.* 38, 129.) According to Bley, the brown-red precipitate which is formed on adding acetate of copper to excess of gallic acid, contains 47·50 p. c. CuO; but if the copper-salt is in excess, it contains 50·95 p. c. CuO (compare p. 404).

*Gallate of Cobalt.—a. Polybasic.* — Oxide of cobalt extracts gallic acid from its aqueous solution. — *b. Basic.* — Obtained by adding hydrated protoxide of cobalt to a boiling solution of gallic acid in such quantity as to leave the liquid still distinctly acid. The salt when dry has a dark bluish red colour. It is permanent in the air. (Büchner.)

| | | | Büchner. |
|---|---|---|---|
| 10 CoO | 376 | 41·59 | 41·61 |
| 42 C | 252 | 27·88 | 27·99 |
| 20 H | 20 | 2·21 | 2·24 |
| 32 O | 256 | 28·32 | 28·16 |
| $CoO,3C^{14}H^{3}Co^{3}O^{10}$ + 11Aq | 904 | 100·00 | 100·00 |

*c. Bibasic.* — When an aqueous solution of acetate of cobalt is evaporated over the water-bath with excess of gallic acid, a light crimson powder separates, increasing in quantity as the acetic acid evaporates. This powder is washed with water and dried over oil of vitriol. When dried at 100°, it becomes continually darker in colour and loses weight. (Büchner; comp. Bley.)

| | | | Büchner. |
|---|---|---|---|
| 2 CoO | 75·2 | 26·74 | |
| 14 C | 84·0 | 29·87 | 29·69 |
| 10 H | 10·0 | 3·56 | 3·51 |
| 14 O | 112·0 | 39·83 | |
| $C^{14}H^4Co^2O^{10}$ + 6Aq | 281·2 | 100·00 | |

*Gallate of Nickel.* — *a. Basic.* — When hydrate or carbonate of nickel is added to a boiling aqueous solution of gallic acid, various basic compounds are formed, according as the liquid remains more or less acid. If the liquid is still strongly acid, a dark green heavy powder is obtained, greasy to the touch. (Büchner, comp. Bley.)

| | | | Büchner. |
|---|---|---|---|
| 8 NiO | 300·8 | 34·08 | 33·65 |
| 42 C | 252·0 | 28·54 | 27·93 |
| 26 H | 26·0 | 2·94 | 3·04 |
| 38 O | 304·0 | 34·44 | 35·38 |
| $2C^{14}H^3Ni^2O^{10}$ + $C^{14}H^4Ni^2O^{10}$ + 16Aq | 882·8 | 100·00 | 100·00 |

*b.* 1. The acid filtrate of *a* yields, after evaporation to dryness and extraction of the free gallic acid by alcohol, a coarse brown-green powder. — 2. When acetate of nickel is boiled with excess of gallic acid, a light green powder is precipitated, permanent in the air. (Büchner.)

*Mercurous Gallate.* — Mercurous oxide forms with a hot aqueous solution of gallic acid, a heavy white powder. (Harff.)

*b.* Mercurous nitrate forms with gallic acid or an alkaline gallate, a white precipitate which becomes yellowish during washing and drying. It dissolves in strong nitric acid, and is not decomposed by boiling with water. (Harff.)

| | | | Harff. |
|---|---|---|---|
| 7 $Hg^2O$ | 145·6 | 74·06 | 73·76 |
| 3 $C^{14}H^6O^{10}$ | 51·0 | 26·94 | |
| $2C^{14}H^3Hg^6O^{10}$ + $C^{14}H^5Hg^2O^{10}$ + 7Aq | 196·6 | 100·00 | |

*Mercuric Gallate.* — Obtained by mixing mercuric nitrate with gallic acid or an alkaline gallate. It is red at first, but after washing and drying forms a rust-coloured powder. It dissolves in nitric and in hydrochloric acid.

| | | | Harff. |
|---|---|---|---|
| 8 HgO | 864 | 61·38 | 60·72 |
| 3 $C^{14}H^6O^{10}$ | 510 | 38·62 | |
| 4 HO | 36 | | |
| $2C^{14}H^3Hg^3O^{10}$ + $C^{14}H^4Hg^2O^{10}$ + 12Aq | 1410 | 100·00 | |

*Ammonio-mercurous Gallate.* — Mercurous gallate forms with ammonia a black insoluble powder, containing 87 71 p. c. mercurous oxide. (Harff.)

*Ammonio-mercuric Gallate.* — Dark grey powder containing 73·98 p. c. mercuric oxide. (Harff.)

Gallic acid does not precipitate nitrate of silver.

Gallic acid dissolves readily in *alcohol*, sparingly in *ether*.

It does not precipitate gelatin.—Gelatin is precipitated by a mixture of gallic acid and gum (Pelletier), but the precipitate is less coherent than that produced by tannin. (Mulder.)

Gallic acid does not precipitate vegetable bases.

*Appendix to Gallic Acid.*

## Rufigallic Acid. $C^{14}H^{4}O^{8}$.

ROBIQUET. (1836.) *L'Institut.* 1836, No. 161.—*J. Pharm.* 22, 483.—*Ann. Pharm.* 19, 204.—*J. pr. Chem.* 8, 122.—*Pharm. Centr.* 1846, 634.

When a mixture of 1 pt. gallic acid and 5 pts. oil of vitriol is carefully and gradually heated to 140°, and the somewhat viscid liquid, which has assumed a wine-red colour (p. 402) is poured into water, after cooling, light flakes of ellagic acid separate, together with a heavy, brown-red, granular precipitate. This precipitate is separated by levigation from the lighter flakes, and all the sulphuric acid is washed out from it with water. It amounts to nearly two-thirds of the gallic acid used.

Small shining crystals of a crimson colour. Gives off 10·5 p. c. water at 120°, and then consists of $C^{14}H^{4}O^{8}$ (therefore gallic acid *minus* 2 At. water).

Begins to blacken at 120°, and decomposes at a stronger heat, becoming carbonised and covered with small cinnabar-coloured crystals. It is not decomposed by potash in contact with the air.

It dissolves in 3333 pts. of boiling water. It dissolves in potash-ley, neutralising the alkaline reaction; and the solution, after awhile, deposits coloured crystals very soluble in water which appear to be rufigallate of potash. To fabrics impregnated with alum or iron mordants, it imparts the same shades of colour as madder. The colours thus produced withstand soap but not chlorine.

## Tannomelanic Acid.

PHIL. BÜCHNER. (1845.) *Ann. Pharm.* 53, 271.

Quercitannic acid is added to boiling potash-ley of sp. gr. 1·27, till no more effervescence ensues; and the liquid is boiled with fresh portions of water till a sample saturated with acetic acid remains clear on cooling and no longer deposits crystals of gallic acid; it is then mixed with excess of acetic acid, which gives rise to considerable evolution of carbonic acid. The dry residue obtained by evaporation over the water-bath is freed from acetate of potash and undecomposed gallic acid by treating it with alcohol; then dissolved in water, mixed with acetic acid, and precipitated by neutral acetate of lead; which throws down a black-brown precipitate, forming a fine powder when dry.

| | | | Büchner. |
|---|---|---|---|
| 5 PbO | 559 | 60·64 | 59·99 |
| 36 C | 216 | 23·42 | 22·86 |
| 11 H | 11 | 1·19 | 1·34 |
| 17 O | 136 | 14·75 | 15·81 |
| $3C^{12}H^{3}PbO^{6},2(PbO,HO)$ | 922 | 100·00 | 100.00 |

The calculation is that given by Gerhardt (*Traité*, 3, 876); Büchner gives the formula $C^{14}H^{4}O^{7},2PbO$.

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*Oxygen-nucleus* $C^{14}H^{4}O^{6}$.

## Chelidonic Acid.

$C^{14}H^{4}O^{12} = C^{14}H^{4}O^{6},O^{6}$.

PROBST. (1838.) *Ann. Pharm.* 29. 116.—*Pharm. Centr.* 1839, 209.
LERCH. *Ann. Pharm.* 57, 273.—*J. pr. Chem.* 38, 180, 191.—*Pharm. Centr.* 1846, 449.
HUTSTEIN. *N. Br. Arch.* 65, 23.

*Sources.* In all parts of the *Chelidonium majus*, in small quantity, associated with malic acid and another acid, probably fumaric; most abundant at the flowering time. (Lerch.)

*Preparation.* 1. The fresh or dried herb or the root of *Chelidonium majus* is exhausted with warm water containing carbonate of soda; the clarified liquid (or the recently expressed juice) is supersaturated with nitric acid and precipitated with nitrate of lead, not in excess; the precipitate, after being washed with water, and repeatedly treated with very dilute nitric acid to remove the lead-salt of another acid, is decomposed with hydrosulphate of soda; and the liquid is boiled with sulphide of lead and animal charcoal, the excess of sulphide of sodium being decomposed by an acid. The filtrate is somewhat concentrated and dilute sulphuric acid added as long as chelidonic acid continues to separate; and the filtrate, after further evaporation, deposits an additional quantity. (Probst.) — 2. Lerch coagulates the expressed juice of the herb by boiling, acidulates the filtrate with nitric acid, and precipitates the chelidonic acid by addition of nitric acid not in excess. (If too little nitric acid be added, large yellow flakes separate which settle down but slowly; if too much, no precipitate is formed.) Hutstein uses 1 drachm of nitric acid sp. gr. 1·3 to 2 lbs. of juice. The precipitate, containing colouring matter and a lime-salt which cannot be removed without loss by washing with dilute nitric acid, is suspended in water and decomposed by passing sulphuretted hydrogen through the liquid for several days; and the liquid is neutralised with chalk and evaporated till a crystalline crust forms: it then on cooling deposits the greater part of the lime-salt almost pure, in needles having a silky lustre. From the lime-salt, the pure acid may be obtained by repeated crystallisation from dilute nitric acid; but it is better to decompose it with carbonate of ammonia, and mix 1 pt. of the cold-saturated solution of the ammoniacal salt with 2 pts. of moderately diluted hydrochloric acid; the mixture

then solidifies to a crystalline pulp which may be freed from hydrochloric acid by washing with water, and recrystallised from water. (Comp. Hutstein.)

The hydrated acid thus obtained yields the dry acid when heated to 100° or left over oil of vitriol.

*Properties.* Colourless. Has a very sour taste. (Lerch.)

| | *At* 100°. | | Lerch. |
|---|---|---|---|
| 14 C | 84 | 45·65 | 45·40 |
| 4 H | 4 | 2·17 | 2·36 |
| 12 O | 96 | 52·18 | 52·24 |
| $C^{14}H^{4}O^{12}$ | 184 | 100·00 | 100·00 |

*Decompositions.* 1. The acid dried at 100°, gives off 2·0 p. c. (½ At.) water at 150°. [Is there nothing but water given off, and is the residue still chelidonic acid? L.) If the heat be continued, no further loss takes place short of 210°; but at that temperature the acid sustains a considerable though not determinable loss; between 220° and 225°, decomposition takes place, the residue becoming soft, blackening, and giving off carbonic acid. The black mass, treated with water, yields an acid which crystallises in yellowish crusts. — Chelidonic acid burns with slight detonation when heated in the air. — 2. It is scarcely attacked by strong nitric acid; but moderately dilute nitric converts it, with evolution of nitric oxide and carbonic acid, into another acid; malic acid does not appear to be formed.— 3. Chelidonic acid dissolves without decomposition in cold oil of vitriol; but on the application of heat, the solution becomes yellowish, and gives off gas-bubbles, assumes a fine purple-red colour at the boiling heat, but after long boiling, gives off sulphurous acid and acquires a dull undefinable colour. — 4. When the lime-salt is boiled with potash, oxalic acid is produced. (Lerch.)

*Combinations.* With *Water.—a. Hydrated Chelidonic acid.* — An aqueous solution of chelidonic acid gradually evaporated deposits long silky needles, which give off 12·7 p. c. (3 At.) water at 100° or over oil of vitriol. A boiling solution quickly cooled yields small interlaced needles, which convert the entire liquid into a solid mass, and give off 8·92 p. c. (2 At.) water at 100° or over oil of vitriol. (Lerch.) Crystallised chelidonic acid effloresces in the air even at ordinary temperatures. (Probst, Lerch.)

*b. Aqueous Chelidonic acid.* — The acid dissolves sparingly in cold, more abundantly in hot water, so that the solution solidifies on cooling. (Lerch.) It dissolves in 166 pts. of water at 6° and in 26 pts. of boiling water. (Probst.)

The acid dissolves in hydrochloric and sulphuric acids more abundantly than in water. (Lerch.)

*Chelidonates.* — Chelidonic acid is a strong acid, dissolving zinc and iron with evolution of hydrogen, and expelling carbonic acid from its compounds. The *Chelidonates* are divided into *monobasic*, $C^{14}H^{3}MO^{12}$, *bibasic* or *neutral*, $C^{14}H^{2}M^{2}O^{12}$ (see vii. 204), *tribasic* $C^{14}HM^{3}O^{12},HO$ or $C^{14}H^{2}M^{2}O^{12},MO$, and *acid salts* $C^{14}H^{3}MO^{12} + C^{14}H^{4}O^{12}$.

The *bibasic* chelidonates are formed when the acid is neutralised with a metallic oxide or a carbonate; with alkalis or their carbonates, tribasic salts are apt to form. Most of the bibasic salts are soluble in water and crystallisable; they contain several atoms of water, which are given off at or above 150°; the ammonia and silver salts however become anhydrous at 100°. Those which contain colourless bases are themselves colourless. They have no action upon litmus. — The *monobasic* salts are produced by heating the bibasic salts with about ½ of their weight of free chelidonic acid or a dilute mineral acid. If the acid is in excess, acid salts are produced. The monobasic salts are resolved by repeated recrystallisation into acid and bibasic salts. — The *tribasic* salts are formed by treating the bibasic salts with a caustic alkali or alkaline carbonate. Those which contain colourless bases have a fine lemon-yellow colour; those which are soluble impart a deep colour to the water. Most of them contain several atoms of water, which do not escape at 100°. They have no reaction upon litmus. They are decomposed by continued contact with water; those of the alkalis absorb carbonic acid from the air and yield a bibasic chelidonate and a carbonate. — The existence of these tribasic salts has given rise to the supposition that chelidonic acid is a tribasic acid (vid. Gerhardt, *Traité*, 3, 758) [perhaps correctly, even though there is no known salt to which the formula $C^{14}HM^3O^{12}$ can be positively assigned. L.]. According to Berzelius, who assumed a hypothetical anhydrous chelidonic acid = $C^{14}H^2O^{11}$, the bibasic chelidonates treated with caustic alkalis or alkaline carbonates yield a new acid, *chelidinic acid*, which in the hypothetical anhydrous state is $C^{14}H^2O^{10}$, and is reconverted into chelidonic acid, as soon as the third atom of base united with it finds an opportunity of uniting with another acid, even if as feeble as carbonic acid. *Lehrb.* 5, 293.)

The *acid* chelidonates crystallise from the solutions of the bibasic salts in hot hydrochloric acid, in delicate needles or scales which do not give off their water of crystallisation at 100°. They redden litmus, and may be recrystallised, but give up their base when repeatedly treated with hydrochloric acid.

*Chelidonate of Ammonia. — Bibasic.* — A boiling dilute solution of the bibasic lime-salt is neutralised by carbonate of ammonia, and the filtrate evaporated; it then on cooling yields the ammonia-salt in snow-white silky needles. The solution abandoned to spontaneous evaporation, ultimately solidifies to a transparent mass, which when collected and drained on a filter, yields the salt in long capillary crystals resembling a knot of the finest silver-white hair. — It effloresces in contact with the air, gives off 14·23 p. c. (4 At.) water at 100°, and then exactly resembles sulphate of quinine. (Lerch.)

| | *At* 100°. | | Lerch. |
|---|---|---|---|
| 14 C | 84 | 38·53 | 33·87 |
| 2 N | 28 | 12·85 | |
| 10 H | 10 | 4·58 | 4·72 |
| 12 O | 96 | 44·04 | |
| $C^{14}H^2(NH^4)^2O^{12}$ | 218 | 100·00 | |

The salt does not give off ammonia, either when exposed to the air at ordinary temperatures, or when heated to 100°. Heated above 160°, it turns brownish and gives off carbonate of ammonia; the residue does not contain any other acid. By repeatedly evaporating the solution and redissolving the residue, it is converted into the acid salt. It does not form a tribasic salt when treated with carbonate of ammonia or caustic ammonia. (Lerch.)

*Chelidonate of Potash.* — *a. Tribasic.* — 1. The concentrated solution of the bibasic salt is coloured yellow by potash and solidifies in a crystalline mass. — 2. When alcoholic potash is added to an alkaline solution of the salt *b*, the yellow mixture becomes turbid and deposits amber-coloured crystals of the tribasic salt, which, when repeatedly washed with warm alcohol, bake together into a soft amber-coloured mass, which, if dissolved in the smallest possible quantity of boiling water, yields crystals on cooling.

Dark yellow; effloresces in the air, but does not react upon litmus. Absorbs carbonic acid from the air, becomes moist, and then exhibits an alkaline reaction. (Lerch.)

*b. Bibasic.* — Obtained by neutralising the acid with carbonic acid; crystallises in small flocculent, aggregated needles; dissolves readily in water. (Probst.)

*Chelidonate of Soda.* — *a. Tribasic.* — Resembles the potash-salt.

*b. Bibasic.* — 1. Obtained by neutralising the acid with carbonate of soda. — 2. The dilute solution of the lime-salt is precipitated by carbonate of soda, avoiding an excess, which would be indicated by the liquid assuming a yellow colour. — Delicate silky needles, which effloresce readily in contact with the air. It gives off 15·5 per cent. (5 At.) of water at 100°, and 5·65 p. c. (2 At.) more between 150° and 160°. (Lerch.) After drying at 100°, it dissolves in 15·5 parts of water at 150°, and much more abundantly in hot water. (Probst.)

| | *At* 150°. | | Lerch. |
|---|---|---|---|
| 2 NaO | 62 | 26·16 | 26·79 |
| 14 C | 84 | 35·44 | 35·38 |
| 3 H | 3 | 1·27 | 1·35 |
| 11 O | 88 | 37·13 | 36·48 |
| $C^{14}H^{3}Na^{2}O^{12}$ + Aq | 237 | 100·00 | 100·00 |

*c. Monobasic.* — The aqueous solution of *a* is mixed with about ½ pt. of chelidonic acid, the mixture boiled, and the needles which separate on cooling, purified by recrystallisation. (Lerch.)

| | *At* 100°. | | Lerch. |
|---|---|---|---|
| NaO | 31 | 12·81 | 12·66 |
| 14 C | 84 | 34·71 | 34·37 |
| 7 H | 7 | 2·89 | 3·16 |
| 15 O | 120 | 49·81 | 49·81 |
| $C^{14}H^{3}NaO^{12}$ + 4Aq | 242 | 100·00 | 100·00 |

*d. Acid* (p. 415). — Delicate needles or scales.

| | *At* 100°. | | Lerch. |
|---|---|---|---|
| NaO | 31 | 7·13 | 7·16 |
| $C^{28}H^{12}O^{28}$ | 404 | 92·87 | |
| $C^{14}H^{3}NaO^{12}, C^{14}H^{4}O^{12}$ + 5Aq | 435 | 100·00 | |

*Chelidonate of Baryta.* — *a. Tribasic.* — The aqueous solution of the salt *b* is mixed with ammonia; the yellow mixture heated and precipitated with chloride of barium; and the lemon-yellow precipitate quickly washed

with water. — Lemon-yellow powder. Does not give off its water of crystallisation at 100°. Absorbs carbonic acid from the air. Sparingly soluble in water, insoluble in alcohol. (Lerch.)

| | *At* 100°. | | Lerch. |
|---|---|---|---|
| 3 BaO | 229·8 | 52·13 | 51·80 |
| 14 C | 84·0 | 19·06 | 18·88 |
| 7 H | 7·0 | 1·58 | 1·72 |
| 15 O | 120·0 | 27·23 | 27·60 |
| $C^{14}H^{2}Ba^{3}O^{12},BaO + 5Aq$ | 440·8 | 100·00 | 100·00 |

*b. Bibasic.* 1. Obtained by neutralising the aqueous acid with carbonate of baryta. — 2. Better: by adding baryta-water to the aqueous acid till the salt separates out. — 3. By double decomposition of the lime-salt with a baryta-salt. — Hard transparent crystalline grains. The solution has no action upon litmus. The salt does not give off any water at 100°. It dissolves very sparingly in water either hot or cold. (Lerch.)

| | *At* 100°. | | Lerch. |
|---|---|---|---|
| 2 BaO | 153·2 | 45·43 | 45·15 |
| 14 C | 84·0 | 24·91 | 24·71 |
| 4 H | 4·0 | 1·19 | 1·25 |
| 12 O | 96·0 | 28·47 | 28·89 |
| $C^{14}H^{2}Ba^{2}O^{12} + 2Aq$ | 337·2 | 100·00 | 100·00 |

*Chelidonate of Strontia.* — Obtained by dissolving carbonate of strontia in the aqueous acid. Crystallises on cooling in slender needles, which after drying appear interlaced like wool. After drying at 200°, it dissolves in 240 pts. of water at 16° (Probst.)

*Acid.* — Slender needles or scales.

| | *At* 100°. | | Lerch. |
|---|---|---|---|
| BaO | 76·6 | 15·94 | 16·26 |
| $C^{28}H^{12}O^{28}$ | 404·0 | 84·06 | |
| $C^{14}H^{2}BaO^{12} + C^{8}H^{4}O^{12} + 5Aq$ | 480·6 | 100·00 | |

*Chelidonate of Lime.* — *a. Tribasic.* — 1. Produced from *b* by boiling with ammonia, almost without change of form. — 2. When the solution of *b* is mixed with lime-water, no action takes place in the cold, but at the boiling heat, the liquid assumes a yellow colour, the alkaline reaction of the lime-water disappears, and a yellow precipitate separates; the addition of lime water must be continued till the liquid remains alkaline. — An admixture of carbonate of lime is unavoidable. — 3. Prepared like the baryta-salt. — Yellow powder, soft to the touch, sparingly soluble in water, insoluble in alcohol. (Lerch.)

| | *At* 100°. | | Lerch. |
|---|---|---|---|
| 3 CaO | 84 | 28·47 | 28·88 |
| 14 C | 84 | 28·47 | 28·84 |
| 7 H | 7 | 2·37 | 2·75 |
| 15 O | 120 | 40·69 | 39·53 |
| $C^{14}H^{2}Ca^{3}O^{12},CaO + 5Aq$ | 295 | 100·00 | 100·00 |

*b. Bibasic.* — Occurs in the herb of *Chelidonium majus.* For the preparation, see page 413.) Gives off 5 At. water at 150°, the sixth at 200°, in all 18·62 p. c. (6 At.) It dissolves sparingly in cold, abundantly in boiling water, whence it crystallises for the most part on cooling; it is insoluble in alcohol.

| *At* 200°. | | | Lerch. |
|---|---|---|---|
| 2 CaO | 56 | 25·22 | |
| 14 C | 84 | 37·84 | 37·45 |
| 2 H | 2 | 0·90 | 1·12 |
| 10 C | 80 | 36·04 | |
| $C^{14}H^{2}Ca^{2}O^{12}$ | 222 | 100·00 | |

| *At* 100°. | | | Lerch. |
|---|---|---|---|
| 2 CaO | 56 | 20·29 | 20·28 |
| 14 C | 84 | 30·43 | 30·68 |
| 8 H | 8 | 2·90 | 3·04 |
| 16 O | 128 | 46·38 | 46·00 |
| $C^{14}H^{2}Ca^{2}O^{12}$ + 6Aq | 276 | 100·00 | 100·00 |

| *At* 150°. | | | Lerch. |
|---|---|---|---|
| 2 CaO | 56 | 24·24 | 24·07 |
| $C^{14}H^{8}O^{11}$ | 175 | 75·76 | |
| $C^{14}H^{9}Ca^{2}O^{12}$ + Aq | 231 | 100·00 | |

*c. Acid.* Slender needles or scales.

| *At* 100°. | | | Lerch. |
|---|---|---|---|
| CaO | 28 | 6·62 | 6·52 |
| 28 C | 168 | 39·71 | 39·92 |
| 11 H | 11 | 2·62 | 2·65 |
| 27 O | 216 | 51·05 | 50·91 |
| $C^{14}H^{3}CaO^{12},C^{14}H^{4}O^{12}$ + 3Aq | 423 | 100·00 | 100·00 |

*Chelidonate of Lime and Potash.* — When an undiluted solution of the bibasic lime-salt is mixed with an equivalent quantity of carbonate of lime, 1 At. of lime is precipitated, and a tribasic chelidonate is formed, containing 2 At. calcium and 1 At. potassium. — In a very dilute solution, the whole of the lime is immediately precipitated by carbonate of potash. (Lerch.)

*Chelidonate of Magnesia.* — Obtained by dissolving carbonate of magnesia in hot aqueous chelidonic acid, till the liquid is neutralised. Crystallises on cooling, in bifurcate needles, which effloresce in the air, and after drying at 100°, dissolve in 79 pts. of water at 16°, more readily in hot water. (Probst.)

From a mixture of chrome-alum with an alkaline chelidonate, a salt having a fine bright green colour is precipated on application of heat or addition of ammonia. (Lerch.)

By saturating the aqueous acid with oxide of *zinc,* a liquid is formed, which has an acid reaction, a sweetish astringent taste, and yields

crystals as it cools. These crystals, after drying at 100°, dissolve in 140 pts. of water at 14°, more readily in hot water. (Probst.)

*Chelidonate of Lead.* — *a. Sexbasic.* — The salt *c* mixed with ammonia is added to basic acetate of lead. Dark yellow.

| I. | | | | II. | | | | Lerch at 100°. |
|---|---|---|---|---|---|---|---|---|
| 6PbO | 670·8 | .... | 80·16 | 6PbO | 67·08 | .... | 81·03 | .... 80·06 |
| $C^{14}H^{2}O^{10}$ | 166·0 | .... | 19·84 | $C^{14}HO^{9}$ | 15·70 | .... | 18·97 | |
| $C^{14}H^{2}O^{10}$,6PbO | 836·8 | .... | 100·00 | $C^{14}HPb^{3}O^{12}$,3PbO | 82·78 | .... | 100·00 | |

Calculation I is by Lerch; II by Gerhardt (*Traité*, 3, 763).

*b. Tribasic.* — 1. Obtained by treating *c* with ammonia. — 2. The solution of bibasic chelidonate of lime, mixed cold with basic acetate of lead, yields yellowish white flakes containing 2 At. water, which are given off between 150° and 160°, the salt then turning yellow. If the solutions are mixed at the boiling heat, the anhydrous salt is produced at once in the form of a yellow precipitate. — Lemon-yellow amorphous powder, darker if mixed with *a;* decolorised and decomposed by acids; insoluble in water and alcohol, soluble in lead-salts.

| *Precipitated boiling.* | | | | Lerch. |
|---|---|---|---|---|
| 3 PbO | 335·4 | .... | 66·92 | 67·06 |
| 14 C | 84·0 | .... | 16·75 | 15·90 |
| 2 H | 2·0 | .... | 0·40 | 0·52 |
| 10 O | 80·0 | .... | 15·93 | 16·52 |
| $C^{14}H^{2}Pb^{3}O^{12}$,PbO | 501·4 | .... | 100·00 | 100·00 |

| *Precipitated cold.* | | | | Lerch. |
|---|---|---|---|---|
| 3 PbO | 335·4 | .... | 64·57 | 65·03 |
| $C^{14}H^{2}O^{10}$ | 166·0 | .... | 31·96 | |
| 2 HO | 18·0 | .... | 3·47 | 3·60 |
| $C^{14}H^{2}Pb^{3}O^{12}$,PbO + 2Aq | 519·4 | .... | 100·00 | |

*c. Bibasic.* — When a solution of the lime-salt is mixed with nitrate of lead, the liquid becomes turbid and deposits small shining crystalline scales or slender needles, which are insoluble in water, and dissolve in lead-salts and in strong nitric acid, but not in fuming nitric acid.

After drying at 100°, it gives off 4·23 p. c. (2 At.) water at 200°. (Lerch.)

| | *At* 200°. | | | Lerch. |
|---|---|---|---|---|
| 2 PbO | 223·6 | .... | 57·40 | |
| 14 C | 84·0 | .... | 21·55 | 20·88 |
| 2 H | 2·0 | .... | 0·51 | 0·68 |
| 12 O | 80·0 | .... | 20·54 | |
| $C^{14}H^{2}Pb^{2}O^{12}$ | 389·6 | .... | 100·00 | |

| | | | Lerch. |
|---|---|---|---|
| 2 PbO | 223·6 | 54·86 | 54·68 |
| 14 C | 84·0 | 20·61 | 20·48 |
| 4 H | 4·0 | 0·98 | 1·03 |
| 12 O | 96·0 | 23·55 | 23·81 |
| $C^{14}H^{2}Pb^{2}O^{12}$ + 2Aq | 407·6 | 100·00 | 100·00 |

When the solution is heated with strong nitric acid, an acid salt is produced, which forms the tribasic salt when treated with alkalis.

*Ferrous Chelidonate.* — The aqueous acid dissolves iron.

*Ferric Chelidonate.* — *a.* The solution of iron in chelidonic acid passes to a higher degree of oxidation during evaporation, and deposits a dingy yellow precipitate. — *b.* The bibasic soda-salt forms with aqueous sesquichloride of iron, a dingy yellow precipitate, somewhat soluble in acetic acid and in excess of sesquichloride of iron; it does not diminish in weight at 100°, and if set on fire at one point, burns away with a sparkling light, leaving charcoal and sesquioxide of iron. (Lerch.)

| | | | Lerch. |
|---|---|---|---|
| $Fe^{2}O^{3}$ | 80 | 32·52 | 32·60 |
| $C^{14}H^{2}O^{10}$ | 166 | 67·48 | |
| $C^{14}H^{2}O^{10},Fe^{2}O^{3}$ | 246 | 100·00 | |

When chelidonate of potash is mixed with excess of sesquichloride of iron, the greater part of the ferric chelidonate remains dissolved; the pale yellow filtrate gradually assumes a darker colour, and ultimately becomes black-brown and opaque, but recovers its pale yellow colour after some time; on heating the liquid, the changes of colour take place more quickly. The dark brown liquid forms with ammonia a rusty brown precipitate, which becomes black when treated with a larger quantity of ammonia (probably from formation of protoxide of iron); the liquid, after having recovered its pale yellow colour, forms with ammonia a red-brown precipitate containing 57·65 p. c. $Fe^{2}O^{3}$, 7·32 C 1·5 H and 33·56 O; the organic substance contained in it corresponds therefore to the formula $C^{7}H^{8}O^{24}$. (Lerch.) [It probably contains nitrogen in the form of ammonia or of an amide.]

*Chelidonate of Copper.* — The hot solution of chelidonate of soda mixed with sulphate of copper, yields by cooling or by slow evaporation, greyish green crystals sparingly soluble in water. (Probst.)

*Chelidonate of Silver.* — *a. Tribasic.* — When the ammoniacal solution of the bibasic lime-salt or tribasic potash-salt is precipitated with nitrate of silver, a lemon-yellow precipitate is formed, which becomes greenish even during filtration, and when dried in vacuo over oil of vitriol, assumes a yellow-brown colour, and is then no longer soluble in ammonia. On mixing the hot solutions, the decomposition takes place still more quickly. In consequence of this tendency to decomposition, the amount of carbon formed by combustion varies by more than 1 per cent.; the percentage of silver-oxide formed varied from 63·08 to 68·85. (Lerch.) [Lerch's formula

$C^{14}H^2O^{10},3AgO$ requires 67·70 per cent. of oxide of silver; the formula $C^{14}HAg^3O^{12}$ requires 68·91 p. c. As the salt decomposes during filtration, the analysis may be expected to give more silver than the formula requires. L.]

*Bibasic.* 1. Obtained by dissolving oxide of silver in chelidonic acid. — 2. When the bibasic lime-salt is precipitated by nitrate of silver, and heated to the boiling point, the salt crystallises on cooling from the resulting solution, and may be purified by recrystallisation. — Long, colourless silky needles, resembling acetate of silver. Permanent in the air at ordinary temperatures, and not altered by heating to between 100° and 130°. Between 140° and 150°, it decomposes with slight detonation. It dissolves in water, ammonia, and strong nitric acid, but not in alcohol.

| *Anhydrous.* | | | *Hydrated.* | | | Probst. | Lerch. |
|---|---|---|---|---|---|---|---|
| 2 AgO | 232 | 58·29 | 2 AgO | 232 | 57·00 | 56·5 | 57·00 |
| 14 C | 84 | 21·11 | 14 C | 84 | 20·64 | | 20·48 |
| 2 H | 2 | 0·50 | 3 H | 3 | 0·74 | | 0·78 |
| 10 O | 80 | 20·10 | 11 O | 88 | 21·62 | | 21·74 |
| $C^{14}H^2Ag^2O^{12}$ | 398 | 100·00 | + Aq | 407 | 100·00 | | 100·00 |

*Chelidonate of Silver and Calcium.* — On mixing a concentrated ammoniacal solution of the bibasic lime-salt with a concentrated solution of nitrate of silver, a light yellow precipitate is formed, which alters but little in drying, and is decomposed by water only after continued boiling. (Lerch.)

| *Anhydrous.* | | | *Hydrated.* | | | Lerch. |
|---|---|---|---|---|---|---|
| 2 AgO | 232 | 56·63 | 2 AgO | 232 | 54·47 | 54·04 |
| CaO | 28 | 6·72 | CaO | 28 | 6·57 | |
| 14 C | 84 | 20·14 | 14 C | 84 | 19·72 | 19·76 |
| H | 1 | 0·24 | 2 H | 2 | 0·47 | 0·76 |
| 9 O | 72 | 17·27 | 10 O | 80 | 18·77 | |
| $C^{14}HCaAg^2O^{12}$ | 417 | 100·00 | + Aq | 426 | 100·00 | |

Chelidonic acid dissolves at 12° in 700 pts. of alcohol of 75 per cent. (Richter, Probst.)

## Meconic Acid.

$$C^{14}H^4O^{14} = C^{14}H^4O^6,O^8.$$

SERTÜRNER. (1805.) *A. Tr.* 13, 1, 234; 14, 1, 47; *Gilb.* 55, 72; 57, 183; 64, 65.
SEGUIN. *Ann. Chim.* 92, 228.
CHOULANT. *Gilb.* 56, 349.
ROBIQUET. *Ann. Chim. Phys.* 5, 282; also *Gilb.* 57, 163.—*Ann. Chim. Phys.* 51, 236; also *J. Pharm.* 19, 67; also *Ann. Pharm.* 5, 90.—*Ann. Chim. Phys.* 53, 425; also *J. Pharm.* 20, 79. — *Pharm. Centr.* 1833, 209.
A. VOGEL. *Schw.* 20, 196; *Repert.* 4, 40.
JOHN. *Berl. Jahrb.* 1819, 156.
LIEBIG. *Pogg.* 31, 168; also *Ann. Pharm.* 7, 37.—*Ann. Pharm.* 26, 11 3 and 147.—*Pharm. Centr.* 1834, 202.

WACKENRODER. *N. Br. Arch.* 25, 167.—*Pharm. Centr.* 1841, 474, 586.
STENHOUSE. *Phil. Mag. J.* 25, 596; also *Mem. Chem. Soc.* 2. 113; also *Ann. Pharm.* 51, 231; also *J. pr. Chem.* 33, 353.—*Pharm. Centr.* 1844, 129.
H. HOW. *Edinb. Phil. Trans.* 20, 401.—*Ann. Pharm.* 83, 250.

***Mohnsäure, Opiumsäure, Acide meconique.***—In opium and in unripe poppy-heads [? L.].—Discovered by Sertürner, but the more exact investigation has been made principally by Robiquet and by Liebig.

*Preparation.* 1. The aqueous decoction of opium is treated with ammonia to precipitate the morphine; the filtrate concentrated; a small additional quantity of morphine precipitated by ammonia, the filtrate diluted with water and precipitated by chloride of barium; the precipitate, consisting of meconate of baryta, brown colouring matter, and a small quantity of morphine, is mixed with alcohol, and decomposed by digestion with the exact quantity of dilute sulphuric acid required for that purpose; and the filtrate, after being concentrated by evaporation, is left to evaporate further in vacuo; it then yields coloured crystals of meconic acid. The liquid filtered from the meconate of baryta yields when evaporated, a further quantity of the same salt. (Sertürner.)

In consequence of this solubility of the meconate of baryta, the product is but small (Robiquet). An excess of sulphuric acid chars the meconic acid (Pelletier). The hotter and more concentrated the sulphuric acid, and the longer it works, the more completely is the meconic acid converted into comenic acid. If the decoction of opium, after being precipitated by ammonia and filtered, be not well purified before the chloride of barium is added to it, the greater part of the meconate of baryta will remain dissolved (Merck).

2. Pelletier (*Ann. Chim. Phys.* 50, 250) proceeds in the same manner as Sertürner, but uses baryta-water instead of chloride of barium, and removes the greater part of the brown colouring matter from the precipitate by repeated boiling with alcohol.

3. Opium is exhausted with strong alcohol and the tincture mixed with chloride of barium, which precipitates nearly all the meconic acid as nearly pure baryta-salt; this salt is then washed with alcohol and decomposed by sulphuric acid. (Merck, *Repert.* 32, 87.)

4. The filtered decoction of 100 pts. of opium is boiled with 2 pts. of magnesia; the liquid filtered; the grey powder which remains on the filters, freed from colouring matter and morphine by means of hot alcohol; the remaining powder, consisting of basic meconate of magnesia, dissolved in a small quantity of cold very dilute sulphuric acid; the solution precipitated by chloride of barium; the liquid again filtered; and the reddish precipitate of sulphate and meconate of baryta decomposed by long-continued digestion with dilute sulphuric acid; after which the liquid is diluted with a large quantity of water, filtered and evaporated; and the coloured crystals thereby obtained are washed with a small quantity of cold water. (Robiquet) — Or the magnesia-precipitate, after being exhausted with alcohol, is treated with a small quantity of cold very dilute sulphuric acid to remove the excess of magnesia; the liquid is decanted; the residue heated to the boiling point with an excess of a mixture of 1 pt. oil of vitriol and 2 or 3 pts. of water; the liquid filtered at the boiling heat; and the still brown crystals of the acid which separate on cooling are collected. (Robiquet.) [These crystals are probably comenic acid. Gm.)]

5. The decoction of opium freed from morphine by ammonia as in 1, is precipitated by chloride of calcium; and the impure neutral meconate of

lime, amounting to about 8 per cent. of the opium, is carefully washed and suspended in six times its bulk of hot water, then mixed with hydrochloric acid till it is converted into a crystalline powder of pure meconate of lime. 103 pts. of this powder are then decomposed by digestion with water containing 36 pts. of crystallised oxalic acid, and the filtrate is decolorised by animal charcoal. (Winkler, *Repert.* 45, 460.)

6. Opium is exhausted with dilute potash; the filtrate precipitated by chloride of calcium; and the precipitate washed with water and boiling alcohol (according to Robiquet, it is better to exhaust the opium with water at 38°; neutralise the extract with coarsely pounded marble; evaporate to a syrup; mix with concentrated solution of chloride of calcium, whereby the meconate of lime is more completely separated in proportion as the liquids are more concentrated; then wash the precipitate with water and press it). 1 pt. of it is then suspended in a mixture of 3 pts. commercial hydrochloric acid and 20 pts. boiling water; the mixture kept at a temperature short of 100°, and frequently shaken, till the whole is dissolved; and the acid meconate of lime which separates on cooling, is collected on linen, washed with a small quantity of water, and redissolved after pressure in a mixture of 3 pts. of hydrochloric acid and 20 pts. of hot water, avoiding ebullition. The liquid then yields on cooling crystals of meconic acid nearly free from lime, while the mother-liquor, in consequence of the excess of hydrochloric acid, contains scarcely any meconic acid. The still coloured crystals, after being washed and pressed, are dissolved in 16 pts. of hot water; the liquid is strained through linen; and the filtrate is mixed with two-thirds of the original quantity of hydrochloric acid; on cooling it yields crystals of meconic acid free from lime but still coloured. These crystals are suspended in cold water, neutralised with carbonate of potash and heated to 100°, with gradual addition of water in quantity just sufficient to dissolve them; the solution which solidifies on cooling is well pressed (the liquid which runs off yields impure meconic acid when treated with excess of hydrochloric acid); the expressed mass, which is not yet quite white, is redissolved in the smallest possible quantity of boiling water; the solid mass obtained on cooling is again pressed; and this treatment is repeated till a pure white product is obtained. Lastly, this pure meconate of potash is dissolved in 16 to 20 pts. of hot water; the acid meconate of potash which separates on cooling is mixed on linen with a small quantity of cold water, pressed, and redissolved in 16 pts. of hot water; the solution is mixed with 2 or 3 pts. of hydrochloric acid; and the crystals of pure meconic acid which form on cooling are washed with cold water, and recrystallised from solution in the smallest possible quantity of boiling water. (Gregory, *Ann. Pharm.* 24, 43). — The mother-liquor expressed from the potash-salt, still yields a quantity of impure meconic acid when treated with hydrochloric acid. Paper-filters [probably on account of the iron contained in them] cannot be used in any part of the process. (Gregory.) — The chloride of calcium precipitate suspended in ten times its bulk of water is mixed and well stirred up with hydrochloric acid at 90° till the greater part of it is dissolved; the hot liquid is filtered through paper which has been completely freed from iron by hydrochloric acid; the delicate needles of acid meconate of lime which separate on cooling are pressed between linen, dissolved in the required quantity of water at 90°, decomposed by a quantity of hydrochloric acid equal to half that of the chloride of calcium precipitate; and the liquid is heated for a few seconds, but not to 100°, and then left to cool slowly. If lighter crystals of the lime-salt should form above the more densely interlaced crystals of meconic acid, the former may be separated mechanically; or if the crystallisation takes place too rapidly to admit of this mode of separation, the whole must be redissolved in hot water, and the remainder of the lime removed by fresh hydrochloric acid. The crystals of the acid obtained in either way — which should burn away without residue

— are collected on a filter previously purified with hydrochloric acid, washed with cold water, and purified by recrystallisation from hot water; they retain however a brownish colour, which may be removed by treatment with potash &c. according to Gregory's method. (Robiquet.)

How heats the crude acid free from lime with twice its weight of water, till the whole dissolves on addition of ammonia. The solution on cooling solidifies in a crystalline mass which may be freed by pressure from the black mother-liquor, and recrystallised two or three times from the smallest possible quantity of boiling water. From the solution in hot water, the meconic acid separates on addition of excess of hydrochloric acid, in colourless laminæ, which are washed with cold water, and once recrystallised from boiling water.

7. One pt. of opium is macerated, for 24 hours, according to Robinet's method (*J. Chim. méd.* 1, 357), with 6 pts. of a solution of 1 pt. common salt in 4 pts. water; the liquid decanted; the pressed residue again macerated with 3 pts. of a solution of common salt; the liquid decanted from the residue; the residue pressed and repeatedly triturated with cold water; the filtrate evaporated to dryness; and the residue, consisting of a lower brown layer of morphine and extractive matter and an upper yellow layer of meconate of soda, is pulverised, and repeatedly treated with alcohol, which dissolves the former substances and leaves the meconate of soda. This salt is dissolved in water; the solution precipitated by basic acetate of lead; the precipitate decomposed by sulphuretted hydrogen; and the filtrate evaporated. (Merck, *Mag. Pharm.* 15, 147.)

The precipitation of the opium-decoction by means of neutral acetate of lead, proposed by Choulant, Hare (*Phil. Mag. Ann.* 2, 233), and others is rejected by Sertürner, because the oxide of lead carries every thing down with it.

The decoloration of meconic acid by animal charcoal (*Blutlaugenkohle*) though very effectual, is attended with great loss, unless the portion of meconic acid retained by the charcoal is afterwards extracted by carbonate of potash. (Robiquet, Liebig.)

*Properties.* The crystallised acid deprived of its water of crystallisation at 100°, yields a white opaque, effloresced mass. (Robiquet.) Has a sour taste, and reddens litmus strongly.

| *Dried between* 100° *and* 120°. | | | Liebig. | Stenhouse. | Robiquet. |
|---|---|---|---|---|---|
| 14 C | 84 | 42 | 42·3 | 42·45 | 41·01 |
| 4 H | 4 | 2 | 2·0 | 2·07 | 4·49 |
| 14 O | 112 | 56 | 55·7 | 55·48 | 54·50 |
| $C^{14}H^{4}O^{14}$ | 200 | 100 | 100·0 | 100·00 | 100·00 |

*Decompositions.* 1. The acid is resolved at a moderate heat into carbonic acid and comenic acid;

$$C^{14}H^{4}O^{14} = C^{12}H^{4}O^{10} + 2CO^{2}.$$

at a higher temperature, partly into carbonic and pyromeconic acids, partly into water, acetic acid, empyreumatic oil, and charcoal.

The acid, after drying at 120°, gives off water at 170°, which increases in quantity at 220°, and between 200° and 220° is accompanied by carbonic acid. From 220° to 230°, all evolution of gas ceases and

the ash-grey crystalline scaly residue consists of comenic acid [whence comes the water? (Gm.)] If the meconic acid is immediately exposed to a strong heat, it yields at first about 20 per cent. of pyromeconic acid, together with water and acetic acid, then carbonic acid and a very small quantity of combustible gas, together with empyreumatic oil, and at last, long white needles of parapyromeconic acid (a substance requiring further examination), which are difficult to fuse, have a strong acid reaction, are sparingly soluble in water, and likewise redden ferric salts. (Robiquet.)

Dry meconic acid melts between 150° and 200°, and is converted, with frothing and evolution of pyromeconic [and carbonic] acid, into brown comenic acid, which at 250°, gives off pyromeconic acid, carbonic acid, water, a small quantity of acetic acid and brown empyreumatic oil, then assumes a black brown colour, and ultimately leaves a light combustible charcoal. (Wackenroder.)—Meconic acid subjected to rapid dry distillation suffers the same kind of decomposition as comenic acid, and yields the same substance resembling metagallic acid (xi, 384). (Winckler.)

2. Meconic acid rapidly heated in a spoon boils up, emits dense white fumes having a slight empyreumatic odour, burns easily with a yellow flame, and leaves a small quantity of charcoal. (Wackenroder.)

3. Pulverised meconic acid dissolves in *bromine-water*, with rapid evolution of carbonic acid; and the liquid, after a while deposits beautiful crystals of bromocomenic acid:

$$C^{14}H^4O^{14} + 2Br = C^{12}H^3BrO^{10} + HBr + 2CO^2.$$

When chlorine is passed into the aqueous solution of bibasic meconate of ammonia, the monobasic salt is formed, and chlorocomenic acid remains in the mother-liquor. (How.)

4. Meconic acid is quickly decomposed by nitric acid, the mixture being projected from the vessel if large quantities are used, and a large quantity of oxalic acid is formed. (Robiquet.) When nitrate of silver is precipitated by aqueous meconic acid, nitric acid being added in quantity rather larger than is required to dissolve the meconate of silver, and the liquid warmed, flakes of cyanide of silver separate without any evolution of nitrous acid, and oxalate of silver remains dissolved in the acid liquid. The only products of the reaction are carbonic acid, oxalate of silver, and cyanide of silver, the quantity of which is however less as the excess of nitric acid is greater. (Liebig, *Ann. Pharm.* 5, 286.)

5. Oil of vitriol exerts but a slight decomposing action on meconic acid, sulphurous acid being evolved only after long boiling the liquid, and still retaining its power of reddening ferric salts. (Robiquet.)

6. By boiling with water and aqueous acids, meconic acid is converted, with evolution of carbonic acid, into comenic acid:

$$C^{14}H^4O^{14} = C^{12}H^4O^{10} + 2CO^2.$$

This evolution of carbonic acid is observed even when the acid is dissolved in water; and if the boiling be continued, it goes on for several days, till in fact the transformation into comenic acid is complete, the liquid then acquiring a red-brown colour. When a meconate is boiled with excess of either of the stronger acids diluted with water, this

evolution of carbonic acid is much more rapid, amounting to a kind of effervescence, and the liquid remains colourless. (Robiquet.) Liebig also obtained a dark brown extractive secondary product by boiling meconic acid with water; but on heating the acid with strong hydrochloric acid, brisk effervescence ensued and colourless comenic acid was formed; hence the formation of this acid appears to be independent of that of the brown substance.

8. Meconic acid boiled with a concentrated solution of potash, is resolved into oxalic acid, carbonic acid, and a dark brown substance resembling humic acid. (Wackenroder.)

9. When concentrated aqueous solution of bibasic meconate of ammonia is heated for some hours with excess of ammonia to a temperature below the boiling point, comenamic acid is produced. (How, xi, 393.)

$$C^{14}H^{2}(NH^{4})^{2}O^{14} = C^{12}NH^{4}O^{8} + NH^{3} + 2HO + 2CO^{2}.$$

*Combinations.* With Water. — *a. Crystallised Meconic acid.* — White micaceous crystalline scales (Sertürner, Robiquet); rhombic crystals (Merck). Small right rhombic prisms, having their acute lateral edges very much truncated; cleavage parallel to *n*. (Wackenroder, *J. pr. Chem.* 23, 205.) The crystals give off their water at 100°. (Robiquet.)

| | | | Robiquet. | Liebig. |
|---|---|---|---|---|
| $C^{12}H^{4}O^{14}$ | 200 | 78·74 | 78·5 | 78·6 |
| 6 HO | 54 | 21·26 | 21·5 | 21·4 |
| $C^{14}H^{4}O^{14}$ + 6Aq | 254 | 100·00 | 100·0 | 100·0 |

*b. Aqueous Meconic acid.* — The acid dissolves sparingly in cold water, but in 4 pts. of boiling water; from the hot solution in water containing hydrochloric acid, it crystallises more readily than from pure water. (Robiquet.)

The *Meconates* are either *tribasic* (neutral) = $C^{14}HM^{3}O^{14}$, *bibasic* = $C^{14}H^{2}M^{2}O^{14}$, or monobasic = $C^{14}H^{3}MO^{14}$. (Liebig.) The tribasic salts are yellow; those of the alkalis are produced by mixing the acid with excess of alkali. — [The meconates of the alkalis described by Choulant and cited in many systematic works, appear to have contained pyromeconic acid, inasmuch as they were prepared with an acid obtained by distilling meconate of baryta with boracic acid.] The salts heated with boracic, phosphoric or sulphuric acid, yield a sublimate of pyromeconic acid, but not when heated alone. (Choulont & others.) They redden ferric salts. (Sertürner.) They are less soluble in water than the pyromeconates. (Robiquet.) They are insoluble in alcohol. (Sertürner.)

*Meconate of Ammonia.* — *a. Bibasic.* — Obtained in How's process for preparing meconic acid (p. 424). Slender radiating needles having a silky lustre and acid reaction. (Robiquet.) Contains variable quantities of water of crystallisation and gives off from 6 to 16 per cent. at 100°. (How.) It dissolves readily in water.

| | At 100°. | | How. |
|---|---|---|---|
| 14 C | 84 | 35·89 | 35·51 |
| 2 N | 28 | 11·96 | 12·09 |
| 10 H | 10 | 4·27 | 4·73 |
| 14 O | 112 | 47·88 | 47·67 |
| $C^{14}H^2(NH^4)^2O^{14}$ | 234 | 100·00 | 100·00 |

The aqueous solution may be heated nearly to the boiling point without decomposition (p. 426).

*b. Monobasic.* — When chlorine is passed through the aqueous solution of the salt *a*, hard granular crystals soon collect on the edge of the vessel, and these, when recrystallised from boiling water, form thick needles concentrically grouped. (How.) Sparingly soluble in water. (Robiquet.) Gives off 7·56 p. c. (2 At.) water at 100°. (How.)

| | At 100°. | | How. |
|---|---|---|---|
| 14 C | 84 | 38·70 | 38·57 |
| N | 14 | 6·45 | 6·21 |
| 7 H | 7 | 3·22 | 3·55 |
| 14 O | 112 | 51·63 | 51·67 |
| $C^{14}H^3(NH^4)O^{14}$ | 217 | 100·00 | 100·00 |

*Meconate of Potash.* — *a. Tribasic.* — Produced by adding caustic potash to the solution of *b*. Yellow.

*b. Bibasic.* — Crude meconic acid is heated with water, caustic potash added till the liquid assumes a yellowish green colour, and the resulting glutinous mass is treated with water till it dissolves. The solution coagulates on cooling to a nearly solid pulp, which must be pressed and recrystallised. — Colourless silky needles or laminæ, sparingly soluble in cold, more soluble in hot water. (Liebig, *Handb.* 2, 847.) (For the decomposition see page 425).

*c. Monobasic.* — Separates on mixing a cold-saturated solution of *b* with a small quantity of hydrochloric acid, in slender needles, from which all the potash may be removed by further treatment with hydrochloric acid. (Robiquet.)

*Meconate of Soda.* — *a. Bibasic.* — The impure baryta-salt is digested with aqueous sulphate of soda, the filtrate evaporated, and the crystals washed with alcohol; or the alcoholic tincture of opium is precipitated by acetate of soda and the precipitate mixed with warm alcohol. Granular crystals. (Sertürner.) Slender needles containing water of crystallisation and soluble in 5 pts. of water. (Stenhouse.)

*b. Monobasic.* — Obtained in the preparation (*b*) of meconic acid. Crystalline grains, dissolving with tolerable facility in water, sparingly in aqueous potash and in absolute alcohol. (Robiquet, *J. Chim. med* 1, 364.)

*Meconate of Baryta.* — The pure acid does not precipitate baryta-water. (Robiquet.) It forms with excess of baryta-water, a thick, light yellow gummy precipitate, which is insoluble in water, but soluble in acetic acid; and the bibasic potash-salt forms with chloride of barium, white flakes imperfectly soluble in water, but dissolving readily in acetic acid. (Wackenroder.)

*Bibasic*, $C^{14}H^3Ba^2O^{14}+2Aq$. — Dissolves sparingly in water, readily in baryta-water forming a yellow solution. (Liebig.)

*Meconate of Lime.* — *a.* The aqueous acid forms with excess of lime-water, white flakes soluble in acetic acid.

*b. Bibasic.* $C^{14}H^{2}Ca^{2}O^{14} + 2Aq$. — The solution of the bibasic potash-salt supersaturated with ammonia forms with chloride of calcium a yellow gelatinous precipitate. (Liebig.)

*c. Monobasic.* $C^{14}H^{3}CaO^{14} + 2Aq$. — 1. The aqueous acid stirred up with a solution of chloride of calcium not too dilute, and left to stand for some time, yields a copious precipitate, which is insoluble in water and dissolves but slowly in acetic acid. — 2. Obtained in the preparation of meconic acid (method 6); when freed from admixed gypsum by recrystallisation from boiling water acidulated with hydrochloric acid, it forms brown shining laminæ. (Liebig.) — 3. A mixture not too dilute of bibasic meconate of potash and chloride of calcium, deposits when stirred a crystalline powder, which dissolves slowly in water but quickly in acetic acid. (Wackenroder.)

The lime-salt subjected to dry distillation, does not yield pyromeconic acid, but only empyreumatic products. (Stenhouse.)

*Meconate of Lime and Ammonia.* — Precipitated for the most part together with morphine from the opium-decoction; and remains behind when the morphine is dissolved out by alcohol; another portion remains dissolved in the ammoniacal filtrate and crystallises when it is evaporated. (Robiquet.)

*Meconate of Magnesia.* — The aqueous acid boiled with excess of magnesia forms an easily soluble salt. (Ure, *Schw.* 59, 236.)

*Meconate of Yttria.*—The aqueous acid does not precipitate yttria-salts and when digested with yttria and evaporated, leaves a crust sparingly soluble in water.

*Meconate of Zinc.* — The bibasic potash-salt forms with sulphate of zinc, a copious white precipitate insoluble in water and in sulphate of zinc, very sparingly soluble in acetic, but readily in nitric acid.

*Meconate of Tin.* — The white precipitate formed by the potash-salt in solution of protochloride of tin, dissolves readily in excess of the latter. (Wackenroder.)

*Meconate of Lead.* — Meconic acid added in slight excess to neutral acetate of lead, throws down thick yellowish white flakes, insoluble even in hot water. (Stenhouse.) The flakes are likewise insoluble in acetic acid and in acetate of lead. (Wackenroder.)

| | *Dried at* 100°. | | Stenhouse. | Robiquet. |
|---|---|---|---|---|
| 3 PbO | 336 | 63·76 | 63·40 | 54·10 |
| 14 C | 84 | 15·94 | 16·36 | 21·01 |
| 3 H | 3 | 0·57 | 0·66 | 1·67 |
| 13 O | 104 | 19·73 | 19·58 | 23·22 |
| $C^{14}HPb^{3}O^{14} + 2Aq$ | 527 | 100·00 | 100·00 | 100·00 |

Robiquet does not say how the salt which he analysed was prepared; its composition agrees with the formula $C^{14}H^{2}Pb^{2}O^{14}$: Stenhouse did not succeed in preparing such a salt. On the other hand he obtained more basic salts, containing from 68·4 to 74·7 per cent. of lead-oxide, in the form of deep-yellow precipitates by adding meconate of ammonia to neutral acetate of lead rendered slightly ammoniacal by ammonia.

Ferrous sulphate forms with meconate of ammonia a clear colourless mixture, which, when exposed to the air, quickly becomes turbid and assumes first a yellowish red, then a dark red colour. (Wackenroder.)

*Ferric Meconate.* — Meconic acid and its salts impart a bright red colour to ferric salts even when very dilute, but form no precipitate. (Sertürner.) — The reddening is distinguished from that which hydrosulphocyanic acid produces in ferric salts by the fact that the colour of the latter is lighter and much mixed with yellow. — Ink and writing with ink are also reddened by meconic acid. (A. Vogel.) — The reddening is not destroyed by terchloride of gold (which distinguishes it from that produced by hydrosulphocyanic acid) (A. Vogel); or by boiling with nitric acid and a little alcohol; but quickly by chloride of soda and by nitromuriatic acid. (Wackenroder.) It is also destroyed, the ferric oxide being reduced to ferrous oxide, slowly by sunlight, quickly by protochloride of tin (A. Vogel); slowly by sulphuretted hydrogen, and very little by boiling with sulphurous acid. (Wackenroder). The decolorised liquid slowly recovers its red colour by exposure to the air, immediately when treated with nitrous acid.

Aqueous meconic acid does not act in the cold on recently precipitated ferric hydrate, but dissolves a small quantity of it at a gentle heat, and a considerable quantity at about 80°, chiefly in the form of ferrous oxide, so that the filtrate on cooling deposits ferroso-ferric meconate in the form of a reddish powder. (Stenhouse.)

To obtain ferric meconate in the solid state, the solution of the pulverised acid and of sesquichloride of iron in ether free from water and alcohol are mixed; and the red-brown flakes which, after a few minutes are deposited from the deep red mixture, are washed on a filter and dried. If water is present, blood-red drops of liquid separate instead of flakes. — The brown-red powder thus obtained is much less soluble than it was before drying. It dissolves with tolerable facility in cold water and alcohol, more quickly in hot water or in water containing acid. The blood-red solution is converted by ammonia into a clear yellowish red mixture, whereas potash or soda precipitates the ferric oxide. — The brown-red powder contains in 100 parts: 30·82 $Fe^2O^3$, 26·00 C, 1·85H and 41·33O.

*Ammonio-ferric Meconate.* — On mixing neutral meconate of ammonia with a slight excess of a concentrated solution of ferric sulphate made as neutral as possible, this salt is precipitated in a few hours in the form of a fine, amorphous, crimson powder, which must be washed on the filter with water, as long as the water takes up any sulphuric acid. The powder retains its colour when dried in the air at ordinary temperatures; but at 100°, it becomes red-brown and dull, without however any reduction of the sesquioxide of iron to protoxide. It dissolves sparingly in cold water and alcohol, but very readily in hot or in acidulated water. When the aqueous solution is heated to 50°, part of the sesquioxide of iron is reduced to protoxide, and at 109°, the whole, the liquid being at the same time decolorised. The blood-red solution, if quickly heated, is coloured deep yellow by ammonia, without precipitation, whereas potash, soda, or lime decolorises it, with evolution of ammonia and precipitation of hydrated sesquioxide of iron free from protoxide. (Stenhouse.) — The crimson powder contains in 100 parts: 23·05$Fe^2O^3$, 3·49N, 31·24 C, 2·37H and 39·88 O. (Stenhouse.)

*Cupric Meconate.* *a. Bibasic.* — Bibasic meconate of potash forms with solutions of copper, an emerald-green precipitate which yields very little pyromeconic acid by dry distillation. (Stenhouse.) Wackenroder obtained with sulphate of copper, a bluish white precipitate, insoluble in water, but dissolving slowly in acetic, quickly in nitric acid.

*b. Monobasic.* — The free acid imparts an emerald green colour to aqueous sulphate of copper, and produces after a while a pale yellow precipitate. (Robiquet.) — With acetate of copper, it forms a greenish yellow precipitate, which gives off a large quantity of pyromeconic acid by distillation. (Stenhouse.)

*Mercurous Meconate.* — Mercurous nitrate is precipitated by the potash-salt in thick pale yellow flakes, and by the free acid in white curdy flakes, which are insoluble in water and very sparingly soluble in nitric acid. (Wackenroder.)

*Mercuric Meconate.* — The acid and its potash-salt form with mercuric nitrate, a large quantity of yellowish white curdy flakes, which dissolve readily in nitric acid, acetic acid and common salt, but are insoluble in water and in mercuric nitrate. (Wackenroder.)

*Meconate of Silver.* — *a. Tribasic.* — When neutral nitrate of silver is precipitated by meconic acid exactly neutralised with ammonia, the liquid becomes acid and a yellowish white pulpy precipitate is thrown down. The same salt is obtained by repeatedly boiling the salt *b* with fresh portions of water. After drying, it detonates when heated. It dissolves readily in dilute nitric acid, but is insoluble in water and in acetic acid. (Wackenroder.)

| | *Dried at* 120°. | | | Liebig. |
|---|---|---|---|---|
| 3 AgO | 348 | 66·79 | | 66·34 |
| 14 C | 84 | 16·12 | | 16·10 |
| H | 1 | 0·20 | | 0·24 |
| 11 O | 88 | 16·89 | | 17·32 |
| $C^{14}HAg^{3}O^{14}$ | 521 | 100·00 | | 100·00 |

*b. Bibasic.* — The aqueous acid forms with nitrate of silver, a snow-white precipitate which does not become crystalline when washed with cold water, is converted into *a* by boiling with water, and when heated after drying, melts and decomposes without detonation, leaving 52·28 p. c. of white silver. (Liebig, *Ann. Pharm.* 7, 240.) — Liebig formerly obtained (*Ann. Pharm.* 7, 240) under apparently similar circumstances, a white precipitate, which when washed and dried assumed the form of shining crystalline laminæ, and was decomposed by heat, with slight tumefaction, leaving 49·58 per cent. of white silver.

| | *Dried at* 100°. | | | Liebig. |
|---|---|---|---|---|
| 14 C | 84 | 20·29 | | 20·00 |
| 2 H | 2 | 0·48 | | 0·48 |
| 2 Ag | 216 | 52·18 | | 52·28 |
| 14 O | 112 | 27·05 | | 27·24 |
| $C^{14}H^{2}Ag^{2}O^{14}$ | 414 | 100·00 | | 100·00 |

Meconic acid disolves readily in alcohol (Sertürner), less readily in ether, especially if absolute, (Stenhouse.)

Respecting another acid of opium not yet further examined, *vid.* Pfaff (*N. Tr.* 7, 1, 428).

*Conjugated Compounds of Meconic Acid.*

## Ethylmeconic Acid.

$C^{18}H^{8}O^{14} = C^{4}H^{5}O,C^{14}H^{3}O^{13}$.

H. How. (1852.) *Edinb. Phil. Trans.* 20, 401.—*Ann. Pharm.* 83, 357.

***Ethylomeconic acid, Aethylmekonsäure, Aethermekonsäure.***

*Formation and Preparation.* Hydrochloric acid gas is passed into a solution of meconic acid in absolute alcohol, till the liquid fumes strongly; on cooling, a precipitate forms consisting of thread-like crystals which must be washed with cold water and recrystallised from hot water. If only rectified spirit is used, meconate of ethylmeconic acid separates after a longer time only and in a less crystalline state. The mother-liquor contains biethylmeconic acid.

*Properties.* Small shining square needles. Does not give off any water at 100°. The aqueous solution has a strong acid reaction and coagulates albumen.

| | | | How. |
|---|---|---|---|
| 18 C | 108 | 47·36 | 47·26 |
| 8 H | 8 | 3·50 | 3·71 |
| 14 O | 112 | 49·14 | 49·03 |
| $C^{18}H^{8}O^{14}$ | 228 | 100·00 | 100·00 |

*Decompositions.* 1. Melts at 158° or 159°, into a transparent yellow liquid, yielding at the same time a sublimate consisting of shining rhombic crystals. — 2. With alcoholic ammonia, it forms meconamic acid; caustic ammonia in excess decomposes it rapidly. — 3. Heated with alkalies it yields meconates.

*Combinations.* Ethylmeconic acid dissolves readily in water.

It expels carbonic acid from the carbonates with efflorescence. The *Ethylmeconates* are *bibasic* (neutral) $= C^{18}H^{6}M^{2}O^{14}$ or *monobasic* (acid) $= C^{18}H^{7}MO^{14}$:—the acid appears also to form salts with excess of base.

*Ethylmeconate of Baryta.* — *a. Bibasic.* — When the boiling aqueous solution of the acid is exactly saturated with carbonate of baryta, the filtrate deposits the salt in small yellow needles.

| | | | How. |
|---|---|---|---|
| 2 BaO | 153·2 | 42·18 | 41·89 |
| $C^{18}H^{6}O^{12}$ | 210·0 | 57·82 | |
| $C^{18}H^{6}Ba^{2}O^{14}$ | 363·2 | 100·00 | |

In other experiments, How obtained from 42 to 44·5 per cent. of baryta, a basic salt having probably been formed together with the above.

*b. Monobasic.* — When carbonate of baryta is gradually added to water in which solid ethylmeconic acid is immersed, the acid quickly

disappears with effervescence. As soon as the effervescence has ceased, the liquid must be quickly filtered from the resulting yellow salt, and the filtrate placed in vacuo. It then deposits a considerable quantity of carbonate of baryta, which must be separated by filtration; and on again leaving the yellowish filtrate to evaporate in vacuo or at a gentle heat, the monobasic salt separates in yellow rhombic crystals which give off water at 100°. It is soluble in water.

| | *At* 100°. | | How. |
|---|---|---|---|
| BaO | 76·6 | 25·92 | 26·17 |
| 18 C | 108·0 | 36·35 | 36·20 |
| 7 H | 7·0 | 2·36 | 2·63 |
| 13 O | 104·0 | 35·19 | 35·00 |
| $C^{18}H^{7}BaO^{14}$ | 295·6 | 100·00 | 100·00 |

The solution of monobasic ethylmeconate of baryta forms with acetate of lead, a yellowish white precipitate; with sulphate of copper, a pale green precipitate; and with sesquichloride of iron, a brown-red precipitate which dissolves with dark red colour in excess of the iron-salt.

*Ethylmeconate of Silver.* — *a.* Ethylmeconic acid heated with excess of silver-oxide forms an insoluble compound.

*b. Monobasic.* — On mixing the aqueous solution of the monobasic baryta-salt with nitrate of silver, a precipitate is formed which when washed and dissolved in boiling water, yields on cooling, small shining crystals united in stellate groups. Remains unaltered in daylight. Gives off 5·24 p. c. (2 At.) water at 100°.

| | *At* 100°. | | How. |
|---|---|---|---|
| 18 C | 108 | 32·23 | 31·92 |
| 7 H | 7 | 2·08 | 2·20 |
| Ag | 108 | 32·23 | 31·94 |
| 14 O | 112 | 33·46 | 33·94 |
| $C^{18}H^{7}AgO^{14}$ | 335 | 100·00 | 100·00 |

Ethylmeconic acid dissolves readily in ordinary *alcohol,* less readily in absolute alcohol, readily in *ether.*

*Meconate of Ethylmeconic acid,* $C^{32}H^{12}O^{28}=C^{18}H^{7}O^{13},C^{14}H^{3}O^{13}+2HO$. — If the alcohol used in the preparation of ethylmeconic acid is not absolute, there is deposited, after the feathery crystals of ethylmeconic acid, a less crystalline precipitate, which sometimes separates also from the mother-liquor of ethylmeconic acid. This precipitate, when purified by repeated solution in a small quantity of hot water, forms a white amorphous powder, very soluble in water.

| | *At* 100°. | | How. |
|---|---|---|---|
| 32 C | 192 | 44·85 | 44·67 |
| 12 H | 12 | 2·80 | 2·92 |
| 28 O | 224 | 52·35 | 52·41 |
| $C^{32}H^{12}O^{28}$ | 428 | 100·00 | 100·00 |

The warm aqueous solution supersaturated with ammonia, turns yellow without separation of meconamate of ammonia; on addition of strong alcohol, the liquid deposits small yellow radiated crystalline tufts. On evaporating to dryness, there remains a substance, only a very small part of which is soluble in water; the soluble portion forms with hydrochloric acid a precipitate consisting of needle-shaped crystals.—When treated with bases, it does not yield salts, but is decomposed more quickly than ethylmeconic acid.

## Biethylmeconic Acid.

$C^{22}H^{12}O^{14} = 2C^4H^5O,C^{14}H^2O^{12}$.

H. How. *Edinb. Phil. Trans.* 20, 401.—*Ann. Pharm.* 83, 357.

***Biethylomeconic acid, Diäthylmekonsäure.***

*Formation and Preparation.* 1. A mixture of meconic acid with absolute alcohol and oil of vitriol is kept in a state of moderate ebullition; and as soon as the residue in the retort has become syrupy, it is poured into a large quantity of cold water, and the rose-coloured precipitate thereby obtained is several times crystallised from water.—When the quantity of sulphuric acid used is rather large, the product appears to consist chiefly of neutral meconate of ethyl $3C^4H^5O,C^{14}HO^{11}$. (How, *N. Edinb. Phil. J.* 1, 212.) —2. The acid mother-liquor obtained in the preparation of ethylmeconic acid and meconate of ethylmeconic acid, is evaporated at 100° as long as acid vapours continue to escape. The residue, which forms a thick oil or viscid mass and crystallises on cooling, is recrystallised two or three times.

*Properties.* Colourless, flattened prisms. Melts in boiling water before dissolving. Has a strong acid reaction and coagulates white of egg.

| | | | How. (1) | How. (2) |
|---|---|---|---|---|
| 22 C | 132 | 51·56 | 51·22 | 51·34 |
| 12 H | 12 | 4·68 | 4·88 | 4·84 |
| 14 O | 112 | 43·76 | 43·90 | 43·82 |
| $C^{22}H^{12}O^{14}$ | 256 | 100·00 | 100·00 | 100·00 |

Melts to a yellowish liquid at 110°. Boiled with aqueous ammonia, it forms *biamidomeconic acid.*

Biethylmeconic acid decomposes carbonates with effervescence. Its neutral salts are $C^{22}H^{11}MO^{14}$.

*Biethylmeconate of Ammonia.* A solution of the acid in strong alcohol, through which dry ammoniacal gas is passed, coagulates to a nearly solid yellowish mass, which, after being pressed and dissolved in hot alcohol, forms on cooling silky needles united in radiated groups, which dissolve readily and with yellow colour in cold water. Acids added to the solution throw down the acid in its original state.

| | *Dried in vacuo.* | | How. |
|---|---|---|---|
| 22 C | 132 | 48·35 | 48·04 |
| N | 14 | 5·12 | 5·46 |
| 15 H | 15 | 5·49 | 5·64 |
| 14 O | 112 | 41·04 | 40·86 |
| $C^{22}H^{11}(NH^{4})O^{14}$ | 273 | 100·00 | 100·00 |

*Biethylmeconate of Baryta.* — The solution of the ammoniacal salt forms with chloride of barium a yellow gelatinous precipitate which is insoluble in water, but dissolves readily in excess of chloride of barium.

| | *At* 100°. | | How. |
|---|---|---|---|
| BaO | 76·6 | 23·68 | 23·54 |
| $C^{22}H^{11}O^{13}$ | 247·0 | 76·32 | |
| $C^{22}H^{11}BaO^{14}$ | 323·6 | 100·00 | |

The *strontia* and *lime* salts resemble the baryta-salt. In a solution of sulphate of *magnesia*, the ammonia-salt forms a crystalline precipitate; with sulphate of *copper*, a green gelatinous precipitate. *Ferric* salts colour the acid red. With nitrate of *silver*, the ammonia-salt forms a yellow gelatinous precipitate insoluble in boiling water.

Biethylmeconic acid dissolves readily in *alcohol*.

## Meconamidic Acid.

H. How. *loc. cit.*

When a solution of ethylmeconic acid in warm water or alcohol is mixed with aqueous or alcoholic ammonia, the liquid assumes a deep yellow colour and becomes filled with a yellow semi-gelatinous body, which, after washing with dilute alcohol, dries up in the air to an amorphous mass. The solution of this substance in hot water forms with a small quantity of hydrochloric acid, a white precipitate, which dissolves in hot water; and the solution, on cooling, yields meconamidic acid in the form of a white crystalline crust.

| I. | | | II. | | | How. |
|---|---|---|---|---|---|---|
| 84 C | 504 | 39·84 | 14 C | 84 | 42·21 | 39·62 |
| 7 N | 98 | 7·74 | N | 14 | 7·03 | 7·86 |
| 39 H | 39 | 3·08 | 5 H | 5 | 2·51 | 3·29 |
| 78 O | 624 | 49·34 | 12 O | 96 | 48·25 | 49·23 |
| $C^{84}N^{7}H^{39}O^{78}$ | 1265 | 100·00 | $C^{14}NH^{5}O^{12}$ | 199 | 100·00 | 100·00 |

According to How (I), the compound is $C^{84}N^{7}H^{39}O^{72}$ + 6Aq, formed from ethylmeconic acid and ammonia by elimination of alcohol: $6C^{18}H^{8}O^{14} + 7NH^{3} = C^{84}N^{7}H^{39}O^{72} + 6C^{4}H^{6}O^{2}$; according to Gerhardt (II), it is impure meconamic acid $C^{14}AdH^{5}O^{12}$.

Boiled with potash-ley, it gives off ammonia, and the residue contains meconic acid.

*Ammonia-compound.* — For the preparation; vid. sup. — Consists of microscopic round grains or cellules. When dry, it may be rubbed with difficulty to a powder having a fine yellow colour. Dissolves readily in hot water, with evolution of ammonia. Gives off ammonia at 100°, blackens and melts at a stronger heat.

| | | | How. |
|---|---|---|---|
| 84 C | 504 | 36·23 | 36·42 |
| 16 N | 224 | 16·24 | 15·98 |
| 63 H | 63 | 4·52 | 4·78 |
| 75 O | 600 | 48·01 | 42·82 |
| $C^{84}N^{16}H^{63}O^{75}$ | 1391 | 100·00 | 100·00 |

According to How, it is $C^{84}N^{7}H^{24}(NH^{4})^{9}O^{72} + 3Aq$.

When decomposed by hydrochloric acid, it yields a quantity of sal-ammoniac corresponding to 10·4 p.c. (9 At.) of nitrogen.

With baryta-salts it forms a yellow amorphous precipitate insoluble in boiling water; with nitrate of silver, a yellow gelatinous precipitate which blackens in drying;—both of variable composition.

¶. *Oxyamidogen-nucleus* $C^{14}Ad^{2}H^{2}O^{6}$.

## Biamidomeconic Acid.

$C^{14}N^{2}H^{6}O^{10} = C^{14}Ad^{2}H^{2}O^{6},O^{4}$.

H. How. *N. Edinb. Phil. J.* 1, 212; *Pharm. Centr.* 1855, 369; *Liebig and Kopp's Jahresber.* 1855, 494.

When biethylmeconic acid is boiled with ammonia, biamidomeconic acid separates and alcohol is evolved:

$$2C^{4}H^{5}O,C^{14}H^{2}O^{12} + 2NH^{3} = C^{14}N^{2}H^{6}O^{10} + 2C^{4}H^{6}O^{2}.$$

Greyish white powder, which has a strong acid reaction and expels carbonic acid from its salts. It is readily decomposed by caustic alkalis. Dissolves with difficulty in cold water and in dilute acids.

May be regarded as bibasic meconate of ammonia *minus* 4 At. water:

$$C^{14}H^{2}(NH^{4})^{2}O^{14} - 4HO = C^{14}N^{2}H^{6}O^{10}.\ ¶.$$

*Oxyamidogen-nucleus* $C^{14}AdH^{5}O^{4}$.

## Gallamic Acid.

$C^{14}NH^{7}O^{8} = C^{14}AdH^{5}O^{4},O^{4}$.

W. Knop. *Pharm. Centr.* 1854, 857; 1855, 657, 741.

*Gallaminsäure, Gallussäureamid.*

*Preparation.* A boiling solution of 3 oz. of tannic acid from Chinese gall-nuts in the requisite quantity of water, is treated with a mixture

containing, to every 5 oz. of strong ammonia, the quantity of acid sulphite of ammonia obtained from 3 drams of the carbonate, the proportions being so adjusted that the liquid may still smell distinctly of ammonia; and the liquid is kept in a state of brisk ebullition till it begins to turn thick. After the solution has cooled to 40°, sulphurous acid gas is passed into it, whereupon gallamic acid separates, and causes the whole to solidify into a crystalline pulp. The mother-liquor contains the hydrylaminamide of paragallic acid and probably also that of ellagic acid.

*Properties.* Colourless crystalline laminæ having a fatty lustre. Reddens litmus. After drying at 90°, it does not give off any water at 100°.

| | | | Knop. |
|---|---|---|---|
| 14 C | 84 | 49·70 | 49·70 |
| N | 14 | 8·28 | 8·17 |
| 7 H | 7 | 4·14 | 4·29 |
| 8 O | 64 | 37·88 | 37·84 |
| $C^{14}NH^7O^8$ | 169 | 100·00 | 100·00 |

*Decompositions.* 1. When boiled for some time with dilute acids, it yields gallic acid and a salt of ammonia. — 2. By boiling with potash-ley it is decomposed in the same manner as gallic acid.

*Combinations.* Gallamic acid dissolves in water mixed with half its quantity of strong hydrochloric acid, and crystallises unaltered on boiling. Decomposition takes place only after continued boiling.

Respecting the crystals first called by Knop *Tannigenamsäure*, then *Gallussäureamid*, then *Gallussäurehydrylaminamid*, but now regarded as a mixture, see *Pharm. Centr.* 1852, 417; 1854, 858; 1855, 661 and 857 (comp. *Tannic acid*).

*Primary-nucleus* $C^{14}H^{12}$.

## Damaluric Acid.

$C^{14}H^{12}O^4 = C^{14}H^{12},O^4$.

STÄDELER. (1850.) *Ann. Pharm.* 77, 27.—*J. pr. Chem.* 52, 44.—*Pharm. Centr.* 1851, 10.

From δάμαλις (a heifer) and ὄυρον.

Occurs in the urine of the cow, of the horse and of man. — When the solution obtained in the preparation of taurylic acid (xi. 154) by agitating the oily mixture of carbolic, taurylic, damaluric and damolic acids with carbonate of soda, is evaporated and distilled with sulphuric acid, a distillate is obtained having the odour of butyric acid, and consisting of a heavy oil and an acid aqueous solution. This distillate boiled with carbonate of baryta yields a filtrate, from which there separate, first crystals of *damolate* of baryta, melting when heated and containing 27·60 p. c. of baryta, — then crystals of *damalurate* of baryta, and lastly, crystals which contain 44·46 p. c. of baryta, and are probably a mixture of damalurate of baryta with the baryta-salt of butyric, valerianic or a peculiar acid.

Damaluric acid is a colourless oil, somewhat heavier than water, and having a peculiar odour like that of valerianic acid. Reddens litmus strongly. Decomposes carbonate of soda.

*Damalurate of Baryta.* — Very small white prisms which when heated, do not melt, but leave carbonate of baryta in the form of the crystals. Blues reddened litmus paper.

| | | | Städeler. |
|---|---|---|---|
| BaO | 76·6 | 39·16 | 39·19 |
| $C^{14}H^{11}O^{3}$ | 119·0 | 60·84 | |
| $C^{14}H^{11}BaO^{4}$ | 195·6 | 100·00 | |

The baryta-salt forms with *basic acetate of lead*, a white precipitate consisting of microscopic needles arranged in spherical groups, and with nitrate of *silver*, a white powder not blackened by light.

| *Silver-salt.* | | | Städeler. |
|---|---|---|---|
| 14 C | 84 | 35·74 | 35·38 |
| 11 H | 11 | 4·68 | 4·68 |
| Ag | 108 | 45·96 | 45·70 |
| 4 O | 32 | 13·62 | 14·24 |
| $C^{14}H^{11}AgO^{4}$ | 235 | 100·00 | 100·00 |

*Oxygen-nucleus* $C^{14}H^{6}O^{6}$.

## Tannoxylic Acid.

$C^{14}H^{6}O^{12} = C^{14}H^{6}O^{6},O^{6}$. ?

PH. BUCHNER. (1845.) *Ann. Pharm.* 53, 369.

*Formation.* By the action of cold potash-ley on quercitannic acid in contact with the air.

*Preparation.* A cold moderately dilute solution of potash is saturated with quercitannic acid, and the solution, after exposure to the air in shallow vessels for some days till it has become blood-red and opaque, is precipitated with neutral acetate of lead. The red precipitate is freed from carbonate of lead by means of acetic acid, the colour then changing to a fine carmine-red; and the admixed tannate of lead is removed by repeated treatment with acetic acid, and finally by boiling with dilute acetic acid, till ammonia no longer forms in it a precipitate of tannate of lead. The tannoxylate of lead is digested with alcohol and a quantity of sulphuric acid, which leaves part of it undecomposed, and the acid mother-liquor is evaporated over the water-bath; it then leaves a red, uncrystallisable syrup, which dries up to a brown-red mass when the evaporation is complete.

The *lead*-salt (preparation above given) has a brick-red, or in the moist state, nearly a carmine-red colour. It dissolves very sparingly in strong boiling acetic acid, forming a reddish solution which deposits reddish flakes on addition of ammonia.

| I. | | | | II. | | | | Büchner. |
|---|---|---|---|---|---|---|---|---|
| 3 PbO | 335·4 | 64·70 | | 11 PbO | 1229·8 | 63·76 | | 63·59 |
| 15 C | 90·0 | 17·36 | | 56 C | 336·0 | 17·42 | | 17·59 |
| 5 H | 5·0 | 0·96 | | 19 H | 19·0 | 0·98 | | 0·94 |
| 11 O | 88·0 | 16·98 | | 43 O | 344·0 | 17·84 | | 17·88 |
| $C^{15}H^{5}O^{11},3PbO$ | 518·4 | 100·00 | | $C^{56}H^{19}Pb^{11}O^{54}$ | 1928·8 | 100·00 | | 100·00 |

Calculation I, is according to Büchner; according to II (Gerhardt, *Tr.* 3, 875), the salt is $4C^{14}H^{4}Pb^{2}O^{12},3(PbO,HO)$, a formula which represents tannoxylic acid as gallic acid + 2O.

*Primary Nucleus* $C^{14}H^{14}$.

## Naphtha. $C^{14}H^{14}$.

LAURENT. (1837.) *Ann. Chim. Phys.* 64, 321.—*Ann. Pharm.* 25, 283.—*J. pr. Chem.* 11, 418.

PELLETIER & WALTER. *J. Pharm.* 26, 554.—*N. Br. Arch.* 24, 151.—*Pharm. Centr.* 1840, 889.

Contained in rock-oil.

*Preparation.* 1. Rock-oil of *Amiano* is subjected to repeated fractional distillation, the operation being stopped in each case as soon as one-third of the liquid has passed over. The volatile portion is rectified over phosphoric acid (p. 439). (Pelletier & Walter.) — 2. The rock-oil is treated with oil of vitriol before distillation. (Pelletier & Walter, p. 439). — 3. The most volatile portion of the empyreumatic oil obtained by repeated fractional distillation of bituminous shale (p. 442), is purified by agitation with oil of vitriol and rectification over hydrate of potash. (Laurent.)

*Properties.* Transparent, colourless, mobile liquid. That which is prepared by the third method has a peculiar empyreumatic odour. The oil obtained by the first method boils between 83° and 88°; by the second, at 90°; by the third, between 80° and 85°. Sp. gr. of the third, 0·714. Vapour-density of the first, 3·3; of the second, 3·42.

| | | | Laurent. | Pelletier & Walter. (1) | (2) |
|---|---|---|---|---|---|
| 14 C | 84 | 85·74 | 84·76 | 85·11 | 85·4 |
| 14 H | 14 | 14·26 | 14·20 | 14·89 | 13·8 |
| $C^{14}H^{14}$ | 98 | 100·00 | 98·96 | 100·00 | 99·2 |

| | Vol. | Density. |
|---|---|---|
| C-vapour | 14 | 5·8240 |
| H.gas | 14 | 0·9702 |
| Naphtha-vapour | 2 | 6·7942 |
| | 1 | 3·3971 |

According to the boiling point (vii, 57), the formula of naphtha should be $C^{14}H^{12}$, which however requires 87·50 p. c. C and 12·50 H: the boiling point calculated from the formula $C^{14}H^{14}$ is 70° (L.).

*Decompositions.* 1. Naphtha takes fire on the approach of a burning body, even at some distance, and burns with a bright, but somewhat sooty flame. (Laurent.) — 2. With *chlorine* in sunshine, it forms hydrochloric acid and condenses. (Laurent.) Chlorine passed through it at a gentle heat converts it into a yellowish oil heavier than water, which burns from a wick, exhaling an odour of horse-radish, cannot be distilled without decomposition, but is not altered by acids or alkalis. — *Bromine* acts in a similar manner. — *Iodine* is abundantly dissolved by naphtha with the aid of heat, and on cooling, the excess of iodine separates in the crystalline form, the naphtha not being perceptibly altered. On treating the chlorine-compound with iodide of potassium, a substance is formed which appears to contain iodine. (Pelletier & Walter.) — 3. Naphtha is but little attacked when heated with nitric acid; but by continued heating, ampelic acid is produced. (Laurent, Pelletier & Walter.) Oil of vitriol, hydrochloric acid and potash do not exert any action upon it. (Laurent.)

Naphtha is slightly soluble in alcohol of 33°. It mixes in all proportions with ether. Caoutchouc immersed in it, swells up and becomes greasy, but does not dissolve. (Laurent.)

## *Appendix to Naphtha.*

***Rock-oil, Steinöl, Bergöl, Bergbalsam, Quirinusöl, Petroleum, Bitumen candidum, Naphte, Bitumine liquide,***—in the purer state, *Naphtha.* — Essentially a mixture of a variable number of volatile oils consisting of C and H in equal numbers of atoms and generally mixed with paraffin. — According to Pelletier & Walter, the naphtha, naphthene and naphthol (*vid. inf.*) obtained from rock-oil by distillation with oil of vitriol, are contained in it ready formed.

Crude rock-oil from *Amiano* of sp. gr. 0·836, yields by repeated rectification in the water-bath at a very gentle heat, about 0·3 per cent. of the purest oil of sp. gr. 0·753 at 16°, which begins to boil at 70°, but does not boil constantly till the temperature rises to 89°; it mixes with cold absolute alcohol in all proportions and dissolves in 7 pts. of alcohol of sp. gr. 0·835. The vapour at 20·3° has a tension equivalent to 7 cub. cent. of mercury. (Saussure, *Bibl. univ.* 1832, 160.)

*Amiano Naphtha* is amber-coloured; of sp. gr. 0·84, very mobile; has a strong but agreeable odour; contains 85·67 p. c. C and 13·17 p. c. H; begins to boil at 125°, and is in full ebullition at 130°, the temperature then rising quickly to 270°, at which point $\frac{2}{3}$ of the liquid have passed over. The distillate obtained between 270° and 300° is yellower and oily, but tolerably mobile; above 300°, there passes over, first an oil which solidifies to a tremulous mass, then a buttery mass, which yields paraffin after the oil has distilled over; and in the retort there remains charcoal having a metallic lustre. By repeatedly rectifying the liquid which distills over between 125° and 270°, taking each time only the first third of the previous distillation, pure naphtha is obtained, boiling at 85°, and amounting to about $\frac{1}{30}$ of the entire quantity of rock-oil. The rectification of the distillate of higher boiling point, accompanied by dehydration with phosphoric acid, does not yield oils of constant boiling point. — When commercial naphtha is mixed with cold oil of vitriol, the

acid becomes red and slightly heated; and the oil decanted therefrom, when again mixed with oil of vitriol, does not become heated or acquire any colour, the sulphuric acid only becoming pale-red; if this treatment be repeated four or five times till the sulphuric acid no longer becomes coloured, the decanted oil may be separated by repeated distillation into oils of tolerably constant boiling point, and with peculiar facility into oils whose boiling points fluctuate about 90°, 115° and 190°. (Vid. *Naphtha, Naphthene* and *Naphthol.*) Amiano naphtha is therefore a mixture of paraffin with at least three oils, naphtha, naphthene and naphthol. (Pelletier & Walter, *J. Pharm.* 26, 549.)

When pure white rock-oil is distilled with 2 pts. of water and lime, the first $\frac{1}{4}$ which passes over boils at 95·7°, is but little attacked by strong sulphuric acid, and becomes inodorous and indifferent to nitric acid when shaken up with water; the next $\frac{3}{4}$ boils at 172°; the last rises gradually to 252°, but, like the first, is colourless, mobile, and not empyreumatic. The residue separated from the water and distilled by itself yields a yellow oil boiling at 310°, which dissolves for the most part with brown colour in strong sulphuric acid, becomes continually thicker, and ultimately leaves a brown oil, from which boiling absolute alcohol extracts paraffin and an unsaponifiable fixed oil; from the residue ether extracts a brown indifferent resin. (Unverdorben, *Schw.* 57, 243.)

Native rock-oil from *Baku* has a sp. gr. of 0·835 and begins to boil at 140°, but cannot be separated into liquids of constant boiling point even by oft-repeated fractional distillation, the distillate obtained at a certain temperature being resolved by subsequent distillation into liquids of higher and lower boiling point. The oil thus obtained is mobile, and after being shaken up with strong sulphuric acid, which takes away an empyreumatic odour, smells agreeably aromatic; it has a sp. gr. of 0·75, begins to boil at 80°, but is in full ebullition only at 130°. — Rock-oil which had been distilled over water in Baku, smelt very much like oil of turpentine, had a specific gravity of 0·8 and boiled at 110°. (Hess, *Pogg.* 36, 417.) — Blanchet and Sell (*Ann. Pharm.* 6, 308), by distilling Persian rock-oil with water and frequently changing the receiver, obtained: 1. A small quantity of liquid of sp. gr. 0·749, boiling at 94°, colourless, and aromatic; 2. Half of the entire quantity, boiling at 138° (on repeating the distillation, the first $\frac{1}{3}$ boils at 118°); 3. An oil boiling at 187°, and having an aromatic odour; 4. After all the water has passed over, a yellowish oil boiling at 220°; on rectifying over lime, the portion which first passes over boils at 215°; sp. gr. 0·849. (For the analysis, see page 442). According to Thomson (*Thoms. Ann.* 15, 307; *Schw.* 29, 374) Persian rock-oil is transparent and colourless, of sp. gr. 0·836, boils at 160°, the colour becoming darker and the boiling point rising to 172°, and contains 82·2 p. c. C and 14·8 H. — Gregory (*J. Pharm.* 21, 536; *J. pr. Chem.* 4, 1) found the rock-oil from Rangoon (Persia) to be dark brown with a tinge of green, buttery at ordinary temperatures, liquid at 40°, of sp. gr. 0·880, with a not unpleasant odour of flowers and smoke. When distilled, it yielded, first a pale, clear, mobile liquid having an agreeable odour, then a viscid pale yellow liquid having a slightly smoky odour, and finally, as the heat on the retort rose to redness, a pale yellow distillate which solidified at ordinary temperatures The second and third distillates contained paraffin as previously found by Christison, the first likewise contained eupione. — ¶ Warren De la Rue & Hugo Müller have examined rock-oil or earth-oil from Burmah, known in commerce as *Burmese naphtha* or

*Rangoon tar* (*Proc. Roy. Soc.* 8, 221; *Chem. Gaz.* 1856, 375). This substance has at ordinary temperatures the consistence of goose-fat; it is lighter than water, has a greenish colour, and a faint, not unpleasant odour. It contains 96 per cent. of volatile constituents. When it was distilled in a current of steam, first at 100°, and afterwards at higher temperatures, 11 per cent. passed over at 100°, consisting entirely of a volatile oil free from solid hydrocarbons; from 110° to 145°, 10 per cent. of liquid nearly free from solid matter; from 160° to the melting point of lead, 20 per cent. of liquid which contained an appreciable quantity of solid matter, but retained its fluidity at 0°; at a higher temperature, 31 per cent. containing sufficient solid matter to cause it to solidify on cooling; and at a still greater degree of heat, 21 per cent. consisting of liquid and solid substances; and finally 3 per cent. of a substance having the consistence of pitch. The portions which distilled above 145° yielded, at the temperature of a freezing mixture, a quantity of solid matter amounting to 10 or 11 p. c. of the crude tar. — The solid products of distillation yielded by fractional crystallisation from alcohol, at least two substances differing in their physical properties, but identical in composition, (either $C^nH^n$ or $C^nH^{n+1}$).—The liquid products of distillation were found to contain benzol, toluol, xylol $C^{16}H^{10}$, cumol $C^{20}H^{12}$, &c. together with other hydrocarbons, apparently, belonging to the series $C^nH^{n+1}$.

*Rock-oil from the Tegernsee* (quirinus oil) is brownish by transmitted, dark olive green by reflected light, viscid in the cold, mobile at 20°, of sp. gr. 0·835 at 20·5°. Has a strong penetrating balsamic odour and but little taste. Yields by fractional distillation: 1. A nearly colourless distillate having a strong odour of flowers and somewhat of oil of turpentine; — 2. A yellowish distillate of less powerful odour, mobile at 9°, and solidifying for the most part at 6°, into a soft crystalline mass which when filtered at 0°, leaves paraffin on the filter, while the greater part runs through; — 3. A reddish yellow thickish mass consisting of a small quantity of oil, paraffin, and a resinous substance; in the residue there remains a difficultly combustible charcoal. (Kobell, *J. pr. Chem.* 8, 205.)

Rock-oil from *Niebylow* near Kalusz in Galicia is of a yellow-brown colour inclining to green, of sp. gr. 0·960, of the consistence of an extract, and not completely fluid below 61°; that from *Truscawice*, of similar colour, sp. gr. 0·890 and thin syrupy consistence, did not yield paraffin by fractional distillation, and was not coloured by nitric acid after rectification; the first portion of the distillate which then passed over boiled at 274°, lost its offensive odour when treated with oil of vitriol, acquiring an agreeable odour like that of flowers, and turning red; when repeatedly distilled with oil of vitriol and a small quantity of nitric acid and washed with potash, it yielded a transparent colourless liquid, having a pleasant odour of flowers, nearly tasteless, of sp. gr. 0·722 at 15°, boiling at 110°, and not altered by acids or alkalis (perhaps eupione). (Torosiewicz, *Repert.* 55, 15.) — Rock-oil from the mineral water of *Trutkowiec*, cannot be obtained of lower specific gravity than 0·720, even by repeated fractional distillation; it boils at 90°; has an agreeable odour, is very inflammable, and burns with a white flame which does not deposit soot. (Torosiewicz, *Repert.* 61, 398.)

The oil obtained from the asphaltiferous limestone of *Travers* by repeated distillation, — after being shaken up with $\frac{1}{10}$ of oil of vitriol, decanted after standing for a week, freed from sulphurous acid, exposed to the air, shaken up with a solution of caustic potash in 20° pts. of

water, then with 9 measures of air; then with 4 or 5 measures of water, then, after the oil has been decanted from the milky liquid, again shaken up with air and water till the water is no longer rendered milky, — becomes as inodorous as a fixed oil. (Saussure.) — When the *empyreumatic oil from bituminous shale* is distilled, it begins to boil at 100°, and the boiling point gradually rises to 300°; but even if the distillates are fractionated at every 20°, and then distilled apart, no oil of constant boiling point is obtained, the boiling point of each fraction varying only 5° from the beginning to the end. The most volatile portion boils from 80° to 85° (p 439); that from 118° to 128° is very like the former, and when several times distilled with strong nitric acid, yields a colourless oil, which boils between 120° and 122°, and is probably $C^{10}H^{16}$ (*q. v.*). The portion which boils at 169° appears to be identical with eupione. (Laurent, *Ann. Chim. Phys.* 64. 321.) [$C^{20}H^{26}$, the boiling of which by calculation should be 165°? L.]. Compare Völckel, (*Ann. Pharm.* 87, 139.)

To purify commercial rock-oil, Böttger agitates 2 lbs. of it with from 4 to 6 oz. of fuming oil of vitriol, and leaves the mixture in a closed vessel, shaking it frequently; the foreign matters are thereby carbonized. On opening the vessel, a large quantity of sulphurous acid escapes; the transparent colourless oil is decanted with a siphon, repeatedly shaken up with water and then with 3 oz. of quick lime in lumps of the size of peas, and then decanted. The oil thus obtained may be used for preserving potassium and sodium. (*Ann. Pharm.* 25, 100.)

*Analyses of Rock-oil:*

| | Saussure. *a.* | Saussure. *b.* | Thomson. | Ure. | Herrmann. |
|---|---|---|---|---|---|
| C | 87·21 | 85·65 | 82·2 | 82·08 | 85·71 |
| H | 12·79 | 13·31 | 14·8 | 12·31 | 14·29 |
| | 100·00 | 98·96 | 97·0 | 94·39 | 100·00 |

| | Dumas. | Blanchet & Sell. *a.* | Blanchet & Sell. *b.* | Fownes. |
|---|---|---|---|---|
| C | 85·92 | 83·88 | 86·43 | 85·83 |
| H | 12·12 | 14·29 | 13·06 | 12·80 |
| | 98·04 | 98·17 | 99·49 | 98·63 |

| | Hess. *a.* | Hess. *b.* | Hess. *c.* | Pelletier & Walter. *a.* | Pelletier & Walter. *b.* | Pelletier & Walter. *c.* | Pelletier & Walter. *d.* | Pelletier & Walter. *e.* |
|---|---|---|---|---|---|---|---|---|
| C | 79·82 to 81·82 | 84·20 | 85·85 | 85·58 | 85·3 | 84·5 | 85·8 | 85·5 |
| H | 13·50 13·20 | 14·27 | 14·51 | 13·17 | 13·4 | 13·4 | 13·3 | 13·4 |
| | 93·32 95·02 | 98·47 | 100·36 | 98·75 | 98·7 | 97·9 | 99·1 | 98·9 |

Saussure analysed rock-oil from Amiano: *a.* By explosion with oxygen gas: *b.* By passing the vapour of the rock-oil rectified at the heat of the water-bath, through a tube filled with copper-turnings, whereby he obtained charcoal and a combustible gas. Thomson burned crude rock-oil, Herrmann rectified oil from Persia of sp. gr. 0·76, with oxide of copper (*Pogg.* 181, 386); Dumas's Persian oil had been left in contact with potassium till the metal remained perfectly bright (*Ann. Chim. Phys.* 50, 239).—The oil *a* analysed by Blanchet & Snell distilled at 94°, *b* at 215° (p. 441); Hess analysed: *a* the first distillate of crude rock-oil; *b* that from Baku distilled over water; *c* rock-oil purified by fractional distillation (p. 441), and agitation with nitric

acid, then with potash, and lastly with strong sulphuric acid. Pelletier & Walter analysed: *a.* Crude rock-oil from Amiano, which began to boil at 125°; *b.* that which distilled between 100° and 115°; *c.* that between 115° and 120°; *d.* that between 120° and 130°; *e.* that between 140° and 150°.

*Decompositions of Rock-oil.* 1. Passed through a red-hot porcelain tube, it yields very dense charcoal having the metallic lustre, an empyreumatic oil containing a crystalline substance in solution, and gases.— 2. Naphtha from Amiano set aside in a bell-jar filled with oxygen over mercury did not absorb any gas in the course of a year, but after 6 years, 1·62 grm.=2·145 cub. cent. had absorbed 9·44 cub. cents. of oxygen, and formed 1·3 cub. cent. of carbonic acid; the oil was still colourless, but a solid deposit had formed on the sides of the vessel, and a fine dust of sulphide of mercury on the surface of the mercury. (Saussure, *Pogg.* 257, 370; *Ann. Pharm.* 3, 157.)— Exposed to air and light, it is very slowly altered and hardens into a substance which is not asphaltum. Oxygen gas saturated with vapour of rock-oil, and mixed with more oxygen, explodes violently when an electric spark is passed through it.— The oil burns in the air with a white flame which deposits a large quantity of soot. (Saussure.) — 3. With *chlorine* gas, it forms hydrochloric acid and a fuming liquid of sp. gr. 0·884, more soluble in alcohol and more easily decomposed by acids [than the original liquid?] (Saussure.) Purified rock-oil from Baku, yields when saturated with chlorine gas, a large quantity of hydrochloric acid and a liquid containing chlorine. (Hess.) It forms with chlorine only a small quantity of hydrochloric acid, the oil not retaining any chlorine. (Serullas.)— 4. *Iodine* acts violently on rock-oil, even at ordinary temperatures. (Guyot, *J. Chim. med.* 12, 487.) With *chloride of iodine,* rock-oil becomes strongly heated, with separation of iodine and strong evolution of hydrochloric acid, part of the hydrogen being replaced by chlorine; the semifluid mass, after being treated with potash, which takes up the iodine, leaves a light yellow liquid heavier than water, with whitish flakes floating upon it. Both the liquid and the flakes, if passed, after being purified by solution in alcohol, through a red-hot tube, yield charcoal, carburetted hydrogen, and a large quantity of hydrochloric acid. (Serullas, *Ann. Chim. Phys.* 25, 313.) — 5. Fuming *nitric acid* imparts to naphtha from Amiano merely a yellowish colour, without further decomposition. (Saussure.) Concentrated and fuming nitric acid acts but slightly on rectified rock-oil. When rock-oil is gradually added to nitro-sulphuric acid cooled by a freezing mixture and left in it, with frequent stirring, for several days, the oil, after being washed with water and then with carbonate of soda, exhibits the properties of nitrobenzol. Previous to the washing with carbonate of soda, the odour of bitter almond oil is disguised by a pungent odour. It seems as if the most volatile portion of rock-oil consisted of oils of similar character to benzol. When non-rectified rock-oil was used, a brown oil was also formed having a penetrating odour of musk. (R. Wagner, *Polyt. Journ.* 136, 311); *comp.* Warren de la Rue, *Repert of Pat. Invent.*, July, 1855, 57. De la Rue & Müller, by treating the most volatile portion of the distillate from Rangoon tar with nitric or nitrosulphuric acid, obtained nitrobenzol, binitrotoluol and ternitroxylol (*Proceedings of the Royal Society*, 8, 221, *comp.* page 440) — The portion of shale-oil which boils between 80° and 150° yields ampelic acid (p. 272) when heated with nitric acid. (Laurent.) — 6. *Chromic acid* exerts a violent oxidising action upon

rock-oil. — If the glow-lamp with asbestos wick be moistened with rock-oil, the oil takes fire when chromic acid is sprinkled upon it, and the resulting chromic oxide becomes intensely red-hot just as when alcohol is used. (Böttger, viii, 243.) — 7. *Oil of vitriol* exerts but a slight decomposing action on Amiano naphtha, and only with the aid of heat. (Saussure.) — When the first distillate of rock-oil from Tegernsee is mixed with ½ pt. of oil of vitriol, and heated to 100°, whereby the acid acquires a dark blue and the oil a pale amethyst colour, the clear oil decanted after cooling smells strongly of sulphurous acid, becomes turbid on the surface by long standing, and yields a small quantity of reddish brown deposit; when decanted, shaken up with caustic potash, then with ¾ of its weight of strong sulphuric acid and ½ pt. of nitre, it leaves in the retort a thick black-brown mass, and yields a nearly colourless distillate which smells strongly of sulphurous acid, acquires a deeper yellow colour by agitation with caustic potash, and if afterwards digested with strong sulphuric acid, colours that liquid dark brown or even amethyst-red, but is decolorised by agitation with potash. It has an agreeable odour, resembling that of flowers and that of oil of turpentine, tastes very aromatic, is mobile, of sp. gr. 0·778, boils between 94° and 96°, with the barometer at 26·7°, burns with a sooty flame, colours strong nitric acid when gently heated with it, giving off red vapours, and when heated with strong sulphuric acid, gradually turns it brown. The liquid portion of the second distillate filtered from the paraffin, leaves when distilled to ¼, a thick brown oil which dissolves sparingly in boiling alcohol. The solution, on cooling, deposits oil and a small quantity of paraffin; the yellowish distillate, which has a pungent odour like that of rancid fat, is for the most part converted, by shaking up with ½ pt. sulphuric acid, into a black mass, a small quantity of oil however remaining. The black mass freed from sulphuric acid by water, dissolves partially in boiling water, leaving a mould-like substance; and the solution when evaporated leaves a shining brittle mass, which gives off ammonia when heated, reddens litmus, dissolves in water, nitric acid and aqueous alcohol, and precipitates metallic salts. When the oil is treated with strong solution of potash, and distilled, the first third of the distillate consists of a yellowish oil, of sp. gr. 10·812, which smells like rancid butter, colours nitric and strong sulphuric acid dark red, and is decomposed by those acids when heated; it dissolves sparingly in boiling alcohol, separating again as the liquid cools.

*Combinations.* 1. Water acquires the odour of rock-oil without dissolving it. Rock-oil from Amiano dissolves when heated $\frac{1}{14}$ of phosphorus and $\frac{1}{12}$ of sulphur, the greater part separating again in the crystalline form as the liquid cools. Of iodine it takes up at most ⅛. — It absorbs 2½ vol. hydrochloric acid gas and an equal quantity of ammoniacal gas. (Saussure.) It absorbs a small quantity of gaseous fluoride of silicium. (Berzelius.) Mixes in all proportions with liquid carbonic acid. (Thilorier.) Absorbs olefiant gas in large quantities. (Hess, *Pogg.* 36, 426.)

It mixes in all proportions in absolute alcohol, dissolves in 5 pts. of alcohol of 41° Bm. and in 8 pts. of 36 Bm. at 12°. Mixes in all proportions with ether and volatile oils. (Saussure.) — Left in contact with alcohol and nitric acid for eight weeks, it does not yield any crystals. (L.) — The oil of sp. gr. 0·87 to 0·93 and having an empyreumatic odour like oil of wax, which passes over first in the distillation of rock-oil,

yields, when shaken up with ½ vol. nitric acid of sp. gr. 1·36, a turbid mixture, the colour of which becomes somewhat lighter after a while, and from which a portion of the nitric acid is deposited, clear and of a yellow colour; with 2 pts. of strong sulphuric acid, it yields a dark brown mixture, on which after two days, a transparent colourless oil floats. It dissolves in 100 pts. of warm alcohol of 0·855, separating for the most part as it cools, and in 2 pts. of ether of 0·75. (Anthon, *Repert.* 54, 77.)

Reichenbach (*Schw.* 69, 19) distilled 50 kilogrammes of coarsely pounded coal from *Ortaware* near Brünn, with water, as long as oil continued to pass over with the watery vapours, repeating the operation eight times, and thus obtained from 400 kil. of material, 150 grms. of oil. The coal-oil thus produced is transparent and greenish yellow; boils at 167°; has a sp. gr. of 0·836; smells and tastes like rock-oil; is not altered by exposure to air and light. It burns without a wick, and with a bright sooty flame. Placed together with iodine under a bell-jar, it absorbs vapour of iodine, becoming brown-red, then turbid, and ultimately clear, a dark oily iodine-compound being then deposited. It dissolves in cold nitric acid of 1·35, acquiring a reddish colour and becoming clear, with separation of a greenish brown deposit. With strong sulphuric acid and potash, it behaves like rock-oil. It does not dissolve in potash-ley of sp. gr. 1·36, but yellowish-red drops form after a while below the oil. It is insoluble in water, which however acquires its odour. It dissolves in 9 pts. of alcohol of sp. gr. 0·84, and readily in ether. With caoutchouc and resins, it behaves like rock-oil.

## Œnanthylene. $C^{14}H^{14}$.

Bouis. (1855.) *N. Ann. Chim. Phys.* 44, 89.
Limpricht. *Ann. Pharm.* 103, 80.

*Formation and Preparation.* 1. By repeatedly distilling œnanthol over anhydrous sulphuric acid. (Bouis.) — 2. By the action of sodium on chloride of œnanthylene. Sodium in small pieces is thrown into chloride of œnanthylene contained in a tubulated retort, and the action is assisted by a gentle heat. As soon as the quantity of separated chloride of sodium becomes so great as to interfere with the action, the liquid must be distilled and the distillate treated with fresh sodium: to remove the last portions of chlorine, the product must be repeatedly rectified over perfectly bright sodium. (Limpricht.)

By (1): colourless oil which floats on water and smells like caproene (oleene, xi, 411); boils at 50°, but the boiling-point does not remain constant (Bouis); — By (2); Transparent colourless liquid, lighter than water, having a peculiar, alliaceous, but not very strong odour; boils at 95°. (Limpricht.)

| | | | Bouis. | Limpricht. |
|---|---|---|---|---|
| 14 C | 84 | 85·71 | 85·38 | 85·9 |
| 14 H | 14 | 14·29 | 14·30 | 14·1 |
| $C^{14}H^{14}$ | 98 | 100·00 | 99·68 | 100·0 |

The product examined by Bouis, agrees in all respects with caproene (xi, 411); the boiling point calculated from the formula $C^{14}H^{14}$ (vii, 57) is 70° [L.].

Soluble in *alcohol.*

## Œnanthol. $C^{14}H^{14},O^2$.

Bussy & Lecanu. (1827.) *J. Pharm.* 13, 62.
Bussy. *N. J. Pharm.* 8, 321.—*Compt. rend.* 21, 84.—*J. pr. Chem.* 37, 92.—*Pharm. Centr.* 1846, 169.
Williamson. *Ann. Pharm.* 61, 38.—*Pharm. Centr.* 1847, 297.
Tilley. *Phil. Mag. J.* 33, 81.—*Ann. Pharm.* 67, 105.—*J. pr. Chem.* 45, 306.—*Pharm. Centr.* 1848, 645.
Bertagnini. *Ann. Pharm.* 85, 281.
Bouis. *N. Ann. Chim. Phys.* 44, 87.

*Œnanthylic Aldide, Œnanthol, Hydride of Œnanthyl.*

*Formation.* By the dry distillation of castor-oil.

*Preparation.* 1. The yellow oily distillate obtained in the dry distillation of castor-oil, is separated from the watery liquid and distilled with five or six times its bulk of water; the distillate consisting of œnanthol, with small quantities of acrolein, œnanthylic acid and oily fatty acids is shaken up with 6 pts. by weight of water, which dissolves out the greater part of the acrolein, and again distilled with pure water, till no more oily liquid remains; this distillate is shaken up with weak baryta-water till it no longer exhibits an acid reaction, then decanted and distilled; and the portion which goes over between 155° and 158°, is collected apart (below 150°, acrolein distils over.) The pure œnanthol thus obtained is dehydrated by chloride of calcium (Bussy, Williamson.)—2. Tilley heats the œnanthol purified by distillation in water, to 100° in the water-bath, and passes carbonic acid through it till the odour of acrolein is entirely destroyed, then distils in the water-bath at 155°, and dries over chloride of calcium.—3. The product of the dry distillation of castor-oil is shaken up with a solution of carbonate of potash, whereby a solution is formed, which, when heated to the boiling point, yields the œnanthol as a separate layer on the surface; this liquid is then removed, and treated with a moderately concentrated solution of bisulphite of soda, which dissolves the œnanthol, and leaves an oily liquid smelling like a fixed oil. The solution on cooling deposits sulphite of œnanthol and soda, which must be dried and decomposed with warm water containing hydrochloric or sulphuric acid. (Bertagnini.)

*Properties.* Transparent, colourless, very mobile. Sp. gr.=0·827. Has a strong, not unpleasant odour and tastes sweet at first, but afterwards persistently sharp. Refracts light strongly. Boils between 155° and 158° (Bussy); 155° and 156° (Williamson). At 155° (Tilley). Vapour-density=4·139 (Bussy); from 4·08 to 5·01. (Bouis.)

| | | | | Bussy. | Williamson. | Tilley. |
|---|---|---|---|---|---|---|
| 14 C | 84 | 73·68 | | 73·49 | 73·40 | 73·81 |
| 14 H | 14 | 12·28 | | 12·28 | 12·40 | 12·60 |
| 2 O | 16 | 14·04 | | 14·23 | 14·20 | 13·59 |
| $C^{14}H^{14}O^2$ | 114 | 100·00 | | 100·00 | 100·00 | 100·00 |

| | Vol. | Density. |
|---|---|---|
| C-vapour | 14 | 5·8240 |
| H-gas | 14 | 0·9702 |
| O-gas | 1 | 1·1093 |
| Œnanthol-vapour | 2 | 7·9035 |
| | 1 | 3·9517 |

Isomeric with butyrone. According to Tilley, it may be regarded, on account of the decomposition by potash and by hydrochloric acid and alcohol (9 & 10) as $C^{14}H^{15}O,C^{14}H^{13}O^3$; but this view is not accordance with the boiling point and vapour-density (vid. p. 23). L.

*Decompositions.* 1. When the liquid is subjected to continued distillation, the boiling point rises and the residue in the retort exhibits a greater amount of carbon. (Tilley, Bouis.) — 2. In contact with the air, it absorbs oxygen and turns sour; when shaken up with oxygen, it may absorb as much as 10 per cent; at the boiling point, the absorption goes on faster. (Bussy.) — When œnanthol, which is kept cool, is gradually mixed with a quantity of *bromine* sufficient to render the brown-red colour permanent, and repeatedly distilled with water, a colourless liquid is obtained, which turns brown when dried by chloride of calcium or over oil of vitriol, and after being freed from dissolved hydrobromic acid by caustic soda, contains 40·90 p. c. C, 6·53 H, and from 44·6 to 45·7 Br. ($C^{14}H^{13}O^2$ requires 43·5 p. c. C, 6·7 H and 41·4 Br.) On distilling it with water, a brown resin remains in the retort. When œnanthol is mixed with *iodine* and *phosphorus*, a violent explosion ensues. (Limpricht.) — 4. Œnanthol is converted by cold nitric acid of ordinary strength into metœnanthol; when distilled with 2 pts. of a mixture of 1 vol. strong nitric acid and 1 vol. water, it is gradually converted into œnanthylic acid. (Bussy.) The distillate still contains small quantities of two other volatile acids [probably caproic acid, L.], and an oil which may be separated by saturating the acid distillate with baryta and distilling; it is lighter than water, smells like French cinnamon, and turns acid in contact with the air; it is therefore probably oil of cinnamon [but oil of cinnamon is heavier than water. (Gm.)] Besides œnanthylic acid, oxalic acid is produced and a reddish yellow resin soluble in alcohol. (Bussy.) When œnanthol is heated with 2 pts. of strong nitric acid, great heat is produced, red vapours are given off, and the greater part of the œnanthol is destroyed. (Bussy.) When œnanthol is added by drops to strong nitric acid contained in a retort, a violent action takes place, and a mixture of nitacrol (ix, 502), œnanthylic acid, caproic acid and nitric acid distils over; the liquid in the retort contains œnanthylic and caproic acids. (Tilley.) — 5. With *chlorine*, œnanthol forms hydrochloric acid and chlorœnanthol. (Williamson.) — 6. Œnanthol dropped upon crystallised *chromic acid* takes fire with violent explosion; dilute chromic acid converts it into œnanthylic acid. (Bussy.) — 7. With fuming *oil of vitriol*, it forms a conjugated acid which yields crystallisable salts with baryta, lime, and oxide of lead. (Bouis.) — 8. When repeatedly distilled over anhydrous phosphoric acid, it yields œnanthylene. (Bouis.) — 9. With *pentachloride of phosphorus*, it becomes strongly heated, and yields a distillate, which when freed from chlorophosphoric acid by repeated washing with water, and from excess of œnanthol by agitation with acid sulphite of soda, consists of nearly pure chloride of œnanthylene $C^{14}H^{14}Cl^2$. (Limpricht.) According to a former statement of Limpricht, the distillate, after being repeatedly distilled with water and dried over oil of vitriol and caustic soda, contained 53·98 p. c. C, 8·70 H. and 31·00 Cl, agreeing with the formula, $C^{20}H^{18}Cl^2O^2$. — 10. Œnanthol dropped upon fused *hydrate of potash*, gives off hydrogen and forms œnanthylate of potash. (Tilley.)

$$C^{14}H^{14}O^2 + KO,HO = C^{14}H^{13}KO^4 + 2H.$$

Heated with from 2 to 6 pts. of hydrate of potash, it forms the so-called hydride of œnanthyl. (Tilley.) — Dilute potash-ley does not act on œnanthol; strong potash-ley, solid hydrate of potash and hydrate of baryta, become heated in contact with it; and convert it into a salt of œnanthylic acid and an oil which smells like anise, or, if, a rather strong heat has been applied, has an empyreumatic odour. (Bussy.) When œnanthol is mixed with a strong aqueous solution of potash, considerable rise of temperature takes place, and a salt of œnanthylic acid is produced, together with an oil, which is decomposed by simple distillation, and after being washed or distilled with water, contains 76·4 p. c. C, and 12·4 p. c. H, and is therefore not œnanthol. Heated with alcoholic potash, œnanthol yields œnanthylic acid and an oil, which, when dried by chloride of calcium, contains 77·1 p. c. C, and 12·7 H. (Williamson.) Limpricht, by boiling œnanthol for several hours with alcoholic potash, obtained œnanthylate of potash and an oil which could not be distilled without decomposition, the boiling point quickly rising to 300°. When it was distilled with water, the oil which first passed over contained, after drying with chloride of calcium, 82·38 p. c. C and 13·67 H; the following portion contained 83·43 p. c. C and 13 43 H. Œnanthol boiled for 18 hours with alcoholic potash, yielded œnanthylate of potash and a yellow syrupy oil, only traces of which passed over on distilling with water. — Bouis found in the portion of the oil boiling between 120° and 140°, obtained by the action of hydrate of potash on œnanthol, 83·70 p. c. C and 14·37 H.

11. In an alcoholic solution of œnanthol, œnanthylate of ethyl is formed by the action of *hydrochloric acid gas.* (Tilley.) — 12. Œnanthol reduces nitrate of silver; when it is mixed with ammonia and nitrate of silver added, a white precipitate is formed, which is reduced by heating, and silvers the vessel. (Bussy.)

*Combinations.* With water. — *a. Hydrate of Œnanthol.* — Moist œnanthol, cooled to 5° or 6°, deposits colourless crystals, which when pressed between paper, yield a brittle mass resembling camphor, smelling like œnanthol, soluble in alcohol and in acetic acid, insoluble in water. (Bussy & Lecanu, Bussy.)

| | | | Bussy. |
|---|---|---|---|
| 14 C | 84 | 68·29 | 68·28 |
| 15 H | 15 | 12·19 | 12·26 |
| 3 O | 24 | 19·52 | 19·46 |
| $C^{14}H^{14}O^{2}$ + Aq | 123 | 100·00 | 100·00 |

*b.* Œnanthol dissolves very sparingly in water, imparting its odour.

*Œnanthol with Ammonia.* — Œnanthol absorbs a large quantity of dry ammoniacal gas, becoming hot and viscid, crystals appearing to form in it; subsequently however it recovers its mobility. (Tilly, Limpricht.) The ethereal solution does not yield crystals when ammoniacal gas is passed into it. (Limpricht.)

*Œnanthol with Bisulphite of Ammonia.* — 1. The compound of œnanthol with ammonia is dissolved in strong alcohol, and the solution is saturated with sulphurous acid gas. It then deposits a crystalline powder, or, if the solution is rather dilute, distinct crystals. — 2. Œnanthol is shaken up with bisulphite of ammonia and the product is dissolved in boiling alcohol, whence the compound is deposited in the crystal-

line state by cooling or evaporation. (Bertagnini.) Small white prisms. (Tilley.) Less crystalline than the potash and soda-compounds; sparingly soluble in water. (Bertagnini.)

| | | | | Tilley. |
|---|---|---|---|---|
| 14 C | 84 | | 43·1 | |
| N | 14 | | 7·1 | 6·8 |
| 17 H | 17 | | 8·7 | |
| 2 S | 32 | | 16·4 | 16·8 |
| 6 O | 48 | | 24·7 | |
| $C^{14}H^{14}O^2,NH^3,2SO^4$ | 195 | | 100·0 | |

Heated on platinum-foil, it melts, gives off white fumes, blackens and burns with flame, giving off the odour of œnanthol. It decomposes gradually in contact with water, or in aqueous or alcoholic solution, more quickly when heated with water, into œnanthol and bisulphite of ammonia. Still more quickly is this decomposition produced by acids. (Tilley.)

*With Bisulphite of Potash.*—When œnanthol is shaken up with bisulphite of potash of 28° to 30° Bm. a pulpy mass is formed which gradually becomes crystalline, and after being dried and dissolved in alcohol yields small needles. It dissolves in warm bisulphite of potash. (Bertagnini.)

*With Bisulphite of Soda.*—When the crude distillate of œnanthol is shaken up with bisulphite of soda of about 27° Bm., a thick crystalline pulp is formed. From a solution of œnanthol in warm dilute bisulphite of soda, the compound separates in crystals. On recrystallising it from boiling alcohol, crystalline laminæ separate, which fill the entire liquid; these are pressed; washed with cold alcohol till they no longer smell of acrolein, and recrystallised from hot water to free them from a small quantity of sulphate.

Crystallised from alcohol it forms aggregated laminæ which have a strong lustre and become white and nacreous when crystallised from water. They are greasy to the touch and have a slight odour of œnanthol. (Bertagnini.)

| | | | | Bertagnini. |
|---|---|---|---|---|
| 14 C | 84 | | 35·59 | 35·77 |
| 17 H | 17 | | 7·20 | 7·17 |
| 2 S | 32 | | 13·55 | 13·47 |
| NaO | 31 | | 13·13 | 13·19 |
| 9 O | 72 | | 30·53 | 30·40 |
| $C^{14}H^{14}O^2,NaO,2SO^2 + 3Aq$ | 236 | | 100·00 | 100·00 |

It is decomposed by chlorine and bromine at ordinary temperatures, by iodine only when heated. When the aqueous solution is heated, œnanthol separates out; the decomposition is accelerated by addition of acids or alkalis, but is not produced by acids without the aid of heat. The compound dissolves readily in water and in warm alcohol, but not in cold alcohol. The aqueous solution forms with barium, lead and silver salts, copious precipitates which contain œnanthol chemically combined. (Bertagnini.)

Œnanthol mixes in all proportions with *alcohol* and *ether*.

## Metœnanthol.

$C^{14}H^{14}O^2$ (or $C^{28}H^{28}O^4$ ?).

BUSSY. *N. J. Pharm.* 8, 321. — *J. pr. Chem.* 37, 96. — *Pharm. Centr.* 1846, 170.

When 1 pt. of œnanthol is shaken up with 2 pts. of ordinary nitric acid at 0°, the liquid acquires a transient rose colour; and on pouring the mixture after 24 hours into a dish and leaving it in a cool place, a beautiful crystallisation like nitrate of ammonia forms on the surface, and sometimes the whole solidifies into a soft unctuous mass. After the acid has been decanted and the mass pressed between paper, a hard brittle substance remains, which may be rendered neutral by repeated melting in hot water.

Between 5° and 6° it is solid, white and inodorous. At higher temperatures it melts into a transparent colourless oil, which boils at 230°; after being heated to the boiling point, it does not solidify till some time after cooling.

| | | | Bussy. |
|---|---|---|---|
| 14 C | 84 | 73·68 | 73·62 |
| 14 H | 14 | 12·28 | 12·27 |
| 2 O | 16 | 14·04 | 14·11 |
| $C^{14}H^{14}O^2$ | 114 | 100·00 | 100·00 |

[Related to œnanthol in the same manner as benzoin to bitter almond oil. L.]

Exposed for several days to a temperature between 10° and 12°, it liquefies, and if kept for a longer time at that temperature, it does not solidify if afterwards cooled even to —12° or —15°, but only when exposed for a considerable time to cold, a moderately low temperature being then sufficient.

Metœnanthol is insoluble in water, dissolves sparingly in cold, more abundantly in boiling alcohol, and crystallises out for the most part on cooling.

## The so-called Hydride of Œnanthyl.

$C^{14}H^{14}O$ or $C^{28}H^{28}O^2$.

TILLEY. (1848.) *Ann. Pharm.* 67, 110.

*Formation and Preparation.* 1 pt. of œnanthol is poured upon 5 or 6 pts. of hydrate of potash, and the mixture is left to stand and heated to 120°, whereupon the liquid becomes thick. A large quantity of water is then added, and the residual oil freed, from every thing soluble in water, is distilled with water; it passes over very slowly, so that the distillation is not completed for several days.

*Properties.* Colourless, mobile oil, having a faint odour of lemons. Boils at 220°, but becomes coloured at the same time and acquires a different odour.

| I. | | | II. | | | Tilley. | |
|---|---|---|---|---|---|---|---|
| 26 C | 156 | 78·79 | 14 C | 84 | 79·24 | 79·28 | 79·43 |
| 26 H | 26 | 13·13 | 14 H | 14 | 13·21 | 13·34 | 13·38 |
| 2 O | 16 | 8·08 | O | 8 | 7·55 | 7·38 | 7·19 |
| $C^{26}H^{26}O^2$ | 198 | 100·00 | $C^{14}H^{14}O$ | 106 | 100·00 | 100·00 | 100·00 |

Perhaps a ketone (Gm.). Therefore probably $C^{26}H^{26}O^2$ (Calc. I.) L. Calculation II is from Tilly's formula.

*Decompositions.* 1. The compound burns with a bright slightly sooty flame. It is difficult to burn with oxide of copper; Tilley's analyses were therefore made with peculiar precaution.— 2. When added by drops to strong nitric acid, it dissolves and oxidises quickly, forming œnanthylic acid, without any secondary product, but not so quickly as œnanthol.— 3. When heated with potash, it gives off hydrogen and yields œnanthylic acid together with a pitch-like substance; the decomposition takes place slowly.

## Œnanthylic Acid. $C^{14}H^{14},O^4$.

LAURENT. (1837.) *Ann. Chim. Phys.* 66, 173.—*Pharm. Centr.* 1838, 280.
TILLEY. *Ann. Pharm.* 39, 160.—*J. pr. Chem.* 24, 237.—*Pharm. Centr.* 1841, 837.—*Ann. Pharm.* 67, 106.—*Pharm. Centr.* 1848, 645.
BUSSY. *N. J. Pharm.* 8, 329.—*J. pr. Chem.* 37, 96.—*Pharm. Centr.* 1846, 170.
SCHNEIDER. *Ann. Pharm.* 70, 112.—*Pharm. Centr.* 1849, 476.
ARZBACHER. *Ann. Pharm.* 73, 200.—*Pharm. Centr.* 1850, 274.
BRAZIER & GOSSLETH. *Ann. Pharm.* 76, 268.—*Pharm. Centr.* 1851, 291.

First obtained by Laurent in an impure state as *azoleic acid*; called *aboleic acid* by Berzelius. Occurs in the fusel-oil of spirit obtained from rice or maize (Wetherill, *Chem. Gaz.* 1853, 282).

*Formation.* By the oxidation of œnanthol in the air or in oxygen gas. By boiling œnanthol with nitric acid (Bussy, Tilley), or with chromic acid (Brazier & Gossleth); by boiling castor-oil with dilute acid (Tilley), or chromic acid. (Arzbächer.) By heating the distillate obtained from castor oil with nitric acid (Schneider, *Ann. Pharm.* 70, 112), or that from oleic acid with strong nitric acid. (Laurent, Redtenbacher, *Ann. Pharm.* 59, 41.) By the action of potash on œnanthol (p. 448).

*Preparation.* 1. One pt. of œnanthol is distilled with 2 pts. of a mixture of 1 vol. strong nitric acid and 2 vol. water till the greater part has passed over; the oily distillate decanted from the acid water is saturated with baryta-water, and evaporated to the crystallising point; and the baryta-salt which crystallises out is decomposed by sulphuric or phosphoric acid: the œnanthylic acid then rises to the surface in the form of a colourless liquid. An additional quantity of œnanthylate of baryta may be obtained by washing the residue in the retort with water, which extracts nitric and oxalic acid, and neutralising with baryta-water. (Bussy.)—2. When œnanthol is distilled with strong nitric acid and the

distillate is mixed with water, nitacrol settles down in heavy drops, whilst an oily mixture of œnanthylic and caproic acids rises to the surface of the aqueous acid; and if this mixture be purified by distillation with water and neutralised with baryta (the yellow colour which the liquid assumes, proceeds from nitrocholic acid); the mixture of the two baryta-salts repeatedly crystallised, and the aqueous solution evaporated till a crystalline film forms on the surface, the œnanthylate of baryta crystallises out first in lancet-shaped laminæ. The mother-liquor is again evaporated and left to cool, till the crystalline pulp becomes mixed with tuft-like crystals of caproate of baryta. (Tilley.) — 3. A mixture of 1 pt. castor-oil and 2 pts. of nitric acid diluted with an equal bulk of water is heated in a retort; a violent action then takes place, so that the retort must be removed from the fire till it diminishes, after which the distillation is continued for several days. The receiver contains the oily acid; while in the retort there remains a watery liquid, and a thick fatty substance which, when distilled with water, yields a large additional quantity of the oily acid. The product is washed with water, distilled with water, and dried by fused phosphoric acid. (Tilley.) — 4. Castor-oil is mixed in a retort with a small quantity of a mixture of 4 pts. bichromate of potash, 5 pts. of oil of vitriol and 12 pts. of water; on heating the mixture, a violent action and frothing takes place; and as soon as the liquid boils quietly, a larger quantity of the warm mixture is added. If the distillation be carefully conducted so that no sulphurous acid forms, the oil first becomes thick, and ultimately solidifies in a black mass. The watery portion of the distillate separated from the oily portion, which also still contains œnanthylic acid, is saturated with carbonate of baryta, evaporated to dryness, and boiled with alcohol. The filtered solution solidifies on cooling into a crystalline mass, which when washed with cold alcohol, and recrystallised from hot alcohol of 88 per cent., yields pure œnanthylate of baryta. (Arzbächer.) This method cannot be recommended for the preparation of œnanthylic acid. (Brazier & Gossleth.)

*Properties.* Transparent colourless oil, having an unpleasant odour like that of codfish, faint in the cold, but becoming stronger at higher temperatures. (Bussy.) Has a peculiar aromatic odour, and a pungent exciting taste. (Tilley.) Begins to boil at 148°, but decomposes and blackens when subjected to continued distillation. (Tilley.) Boils at 212°. (Strecker, *Lehrb.* 5, 96.)

| | | | Laurent. | Tilley. |
|---|---|---|---|---|
| 14 C | 84 | 64·61 | 62·79 | 64·44 |
| 14 H | 14 | 10·77 | 10·71 | 10·71 |
| 4 O | 32 | 24·62 | 26·50 | 24·85 |
| $C^{14}H^{14}O^4$ | 130 | 100·00 | 100·00 | 100·00 |

*Decompositions.* 1. Œnanthylic acid burns with a white flame. (Tilley.) — 2. Heated with soda-ley, it forms a neutral oil. (Arzbächer.) — 3. Heated with potash-lime, it yields gaseous and liquid hydrocarbons of the formula $C^nH^n$. (Cahours, *Compt. rend.* 31, 141) — 4. When distilled with pentachloride of phosphorus, it yields chloride of œnanthyl, which is resolved by water into hydrochloric and œnanthylic acids. Cahours, *Compt. rend*, 25, 724.) — 5. A concentrated solution of œnanthylate of potash decomposed by a current of six Bunsen's cells (xi, 31), gives off hydrogen and carbonic acid gases, while monocarbonate and bicarbonate of potash are formed, and an oil rises to

the surface, which, when distilled with potash, leaves œnanthylate of potash, and yields a distillate consisting mainly of caproyl $C^{24}H^{16}$, and a hydrocarbon $C^{24}H^{24}$ boiling at 170°. (Brazier & Gossleth.)

*Combinations.* Œnanthylic acid dissolves in concentrated nitric acid and is precipitated therefrom by water. — With salifiable bases it forms the *Œnanthylates.*

*Œnanthylate of Ammonia* is very soluble in water. (Bussy.)

*Œnanthylate of Potash.* — Obtained by saturating the acid with carbonate of potash; does not crystallise; is very soluble. (Tilley.)

*Œnanthylate of Baryta* (pp. 451, 452). — White nacreous scales. (Bussy, Williamson, Arzbächer.) Lancet-shaped tables. (Tilley.) Has a very faint, slightly bitter taste; inodorous, but when rubbed between the fingers, it imparts an unpleasant odour of perspiration. (Bussy.) Dissolves in 57 pts. of water at 23° (Bussy); very easily in hot water; still more easily in hot alcohol of 85 per cent., and crystallises out almost completely on cooling. (Arzbächer.) Dissolves in 392 pts. of alcohol (Bussy); insoluble in ether.

| | | | Bussy. | Williamson. | Tilley. *a.* | Tilley. *b.* | Schneider. | Arzb. |
|---|---|---|---|---|---|---|---|---|
| BaO | 76·6 | 38·77 | 38·80 | 38·70 | 38·50 | 38·23 | 39·35 | 39·27 |
| 14 C | 84·0 | 42·51 | 42·68 | 42·45 | 42·52 | 41·68 | | 42·14 |
| 13 H | 13·0 | 6·58 | 6·51 | 6·85 | 6·72 | 6·89 | | 7·02 |
| 3 O | 24·0 | 12·14 | 12·01 | 12·00 | 12·26 | 13·20 | | 11·57 |
| $C^{14}H^{13}BaO^4$ | 197·6 | 100·00 | 100·00 | 100·00 | 100·00 | 100·00 | | 100·00 |

The salt analysed by Bussy was prepared from the acid obtained by 1; Tilley's salt *a* from the acid prepared by 2; *b* from 3; Arzbächer's salt from acid 4; Schneider's salt from the distillate obtained by heating rape-oil with nitric acid; and Williamson's from the acid obtained by the action of potash on œnanthol (p. 448).

*Œnanthylate of Lead.* — The potash-salt forms with acetate of lead a lemon-yellow powder, which is insoluble in water, but slightly soluble in boiling alcohol, whence it separates in small scales on cooling. (Tilley.)

*Œnanthylate of Copper* separates after a while from a mixture of the free acid with acetate of copper in needles having a fine green colour and silky lustre.

*Œnanthylate of Silver.* — The acid neutralised with ammonia forms with nitrate of silver a white precipitate insoluble in water, and turning brown on exposure to light. (Bussy.)

White flakes, which yield by dry distillation an oil and a solid substance, which crystallises in needles from hot alcohol; both are acid.

| | | | Bussy. | Tilley. | Williamson. | Schneider. | Arzb. |
|---|---|---|---|---|---|---|---|
| Ag | 108 | 45·57 | 45·60 | 45·60 | 45·55 | 45·44 | 45·31 |
| 14 C | 84 | 35·44 | 34·82 | 35·38 | 35·20 | | |
| 13 H | 13 | 5·49 | 5·62 | 5·61 | 5·66 | | |
| 4 O | 32 | 13·50 | 13·96 | 13·41 | 13·59 | | |
| $C^{14}H^{13}AgO^4$ | 237 | 100·00 | 100·00 | 100·00 | 100·00 | | |

Œnanthylic acid dissolves in *alcohol* and *ether.*

## Œnanthylate of Ethyl.

$C^{18}H^{18}O^4 = C^4H^5O,C^{14}H^{13}O^3$.

TILLEY. (1841.) *Ann. Pharm.* 39, 162.
WILLIAMSON. *Ann. Pharm.* 61, 38.—*Pharm. Centr.* 1847, 297.

*Preparation.* 1. Hydrochloric acid gas is passed through a solution of œnanthylic acid in strong alcohol; the liquid distilled with aqueous carbonate of potash; and the distillate is washed with water, and finally dehydrated by chloride of calcium in a stream of carbonic acid gas. (Tilley.) 2. Hydrochloric acid gas is passed through a solution of 1 vol. œnanthol in 4 vol. alcohol, till the liquid becomes brownish and fumes strongly, and the œnanthylate of ethyl is then separated by addition of water. (Williamson.)

*Properties.* Colourless oil lighter than water. Solidifies in a freezing mixture. Has a peculiar agreeable odour, and a burning taste. (Tilley.) Has a pleasant fruity odour; distils readily and completely, but with a constantly rising boiling point. (Williamson.)

| | | | Tilley. | Williamson. between 187° and 180°. | Williamson. between 190° and 192°. |
|---|---|---|---|---|---|
| 18 C | 108 | 68·35 | 67·62 | 68·2 | 68·4 |
| 18 H | 18 | 11·39 | 11·57 | 11·7 | 11·3 |
| 4 O | 32 | 20·26 | 20·81 | 20·1 | 20·3 |
| $C^{18}H^{18}O^4$ | 158 | 100·00 | 100·00 | 100·0 | 100·0 |

Burns with a clear non-fuliginous flame.
Insoluble in water, easily soluble in *alcohol* and *ether*.

## Œnanthylate of Phenyl.

$C^{26}H^{18}O^4 = C^{12}H^5O,C^{14}H^{13}O^3$.

CAHOURS. *Compt. rend.* 38, 257.

*Œnanthylsäure Carbolsäure.*

Produced by the action of chloride of œnanthol on phenylic alcohol. Oil boiling between 275° and 280°.

*Appendix to Œnanthylic Acid.*

## Œnanthic Acid.

LIEBIG & PELOUZE. (1836.) *Ann. Pharm.* 19, 246.—*Ann. Chim. Phys.* 63, 113.—*Pogg.* 41, 571.—*Pharm. Centr.* 1837, 23.
MULDER. *Pogg.* 41, 582.—*Pharm. Centr.* 1837, 809.
DELFFS. *Pogg.* 84, 505.—*Ann. Pharm.* 80, 290.—*Pharm. Centr.* 1852, 93.

*Œnanthsäurehydrat, Weinblumensäure, Sitinsäure.*

Produced in the fermentation of wine and grain.

*Preparation.* 1. *Œnanthic ether* is boiled with potash-ley, and the resulting œnanthate of potash is decomposed by dilute sulphuric or hydrochloric acid, the acid then rising to the surface in the form of an oil. It is washed with water, and dried with chloride of calcium or over oil of vitriol. (Liebig & Pelouze, Delffs.) — 2. The fusel-oil obtained in the first distillation of fermented grain is rectified over dilute carbonate of soda; the residue is boiled with water; and the filtered solution is decomposed by dilute sulphuric acid: the acid then collects on the surface of the liquid in the form of a fatty layer which is washed with water, dissolved in alcohol, and the solution left to evaporate. — 3. When rectified fusel-oil is distilled with dilute potash-ley, and the residue is mixed with sulphuric acid, œnanthic acid separates, and may be purified by washing with water and crystallisation from alcohol. (Mulder.)

*Properties.* Dazzling white, soft like butter at 13·2°, above which temperature it melts to a colourless oil. (Liebig & Pelouze.) Buttery mass. (Mulder.) Yellowish oil, which at low temperatures solidifies into an indistinctly crystalline buttery mass. Crystallises from alcohol in a friable mass. Melts even at the heat of the hand, or at all events below 25°. (Delffs.) Tasteless. Inodorous and tasteless. Reddens litmus.

| I. | | | | II. | | | | Liebig & Pelouze. | Mulder. |
|---|---|---|---|---|---|---|---|---|---|
| 14 C | 84 | 68·85 | | 18 C | 108 | 68·35 | | 68·24 | 68·58 |
| 14 H | 14 | 11·48 | | 18 H | 18 | 11·40 | | 11·55 | 11·61 |
| 3 O | 24 | 19·67 | | 4 O | 32 | 20·25 | | 20·21 | 19·81 |
| $C^{14}H^{14}O^{3}$ | 122 | 100·00 | | $C^{18}H^{18}O^{4}$ | 158 | 100·00 | | 100·00 | 100·00 |

Calculation I is from the formula proposed by Liebig. Delffs regards œnanthic acid as identical with pelargonic acid (II), which view agrees with the composition of the barium and silver salts analysed by him, but is opposed by the fact that œnanthic acid is decomposed by heat into water and the so-called anhydrous œnanthic acid. According to this, œnanthic acid should be tribasic, and the formula given by Liebig & Pelouze should be doubled (*comp.* Laurent, *Compt. rend.* 21, 857). Delffs's view is also irreconcilable with the composition of chlorœnanthic acid (p. 460) [and with the boiling point of œnanthic ether. J.L.]. The large variations in the analyses of the salts by Liebig & Pelouze and Mulder and Delffs, show either that those chemists examined different bodies, or that the œnanthates have but little permanence; perhaps they yield pelargonic acid when decomposed. Mulder's analyses agree nearly with the formula $C^{32}H^{11}MO^{6}$ [L.].

*Decompositions.* Œnanthic acid is resolved by heat into water and anhydrous œnanthic acid. (Liebig & Pelouze.) — By very slow evaporation of alcoholic œnanthic acid, *e. g.* in a deep cylindrical glass, hydrated œnanthic acid is obtained as a transparent oil on the surface of the liquid [does not this oil contain alcohol? Gm.], while crystals of the anhydrous acid are formed at the bottom. (Mulder.)

*Combinations.* Mulder assumes the existence of a hydrated œnanthic acid, which he describes as a transparent colourless oil of sp. gr. 0·881, and supposes to be converted into the anhydrous acid by gentle heating or by the action of chloride of calcium. The separation of the hydrated acid into the anhydrous acid and water is also said to be induced by dropping the crystals of the anhydrous acid into the hydrated acid.

| | | | Mulder. |
|---|---|---|---|
| 14 C | 84 | 64·12 | 63·07 |
| 15 H | 15 | 11·44 | 11·15 |
| 4 O | 32 | 24·44 | 25·78 |
| $C^{14}H^{14}O^{3}$ + HO | 131 | 100·00 | 100·00 |

*Œnanthates.* — Œnanthic acid dissolves in the aqueous solutions of the caustic alkalis and their carbonates, and forms mono-acid salts having a basic reaction and bi-acid salts which are neutral. (Liebig & Pelouze.)

*Œnanthate of Ammonia.* — Œnanthic acid dissolves readily in ammonia, and the solution when evaporated leaves a greasy soapy mass, which no longer forms a clear solution in water. (Delffs.)

*Bi-œnanthate of Potash.* — When warm aqueous potash is neutralised with œnanthic acid, the solution solidifies on cooling into a pulpy mass consisting of slender needles which have a silky lustre when dry. (Liebig & Pelouze.)

*Œnanthate of Soda.* — The acid dissolves in boiling carbonate of soda, with evolution of carbonic acid; on boiling the mass with alcohol, the filtered solution yields beautiful, silver-white, shining needles. (Mulder.) When the solution of œnanthic acid in boiling carbonate of soda is evaporated, and the residue boiled with alcohol, the liquid solidifies on cooling into a gelatinous translucent mass. (Liebig & Pelouze.)

*Œnanthate of Baryta.* — Baryta-water is boiled with a slight excess of œnanthic acid, and the crystals first obtained are recrystallised from boiling water. Small crystalline laminæ having a fatty lustre, and feeling like mica. Contains 33·87 p. c. BaO, corresponding with the formula $C^{18}H^{17}BaO$. (Delffs.) (*Calculation*, 33·78 p. c.)

*Œnanthate of Lead.* — Œnanthic acid forms with an alcoholic solution of acetate of lead at ordinary temperatures, thick white flakes of an insoluble acid salt, which melts in hot water, dissolves readily in alcohol, and crystallises from the saturated hot solution. When washed with cold alcohol it is resolved into a hyperacid and a basic salt. — Acetate of lead mixed with œnanthate of soda, forms a precipitate which when dried in vacuo, contains from 38·86 to 39·48 per cent. (Liebig & Pelouze.)

An alcoholic solution of œnanthate of soda forms with acetate of lead, a precipitate containing 27·1 per cent. of oxide of lead. (Mulder.)

*Œnanthate of Copper.* — Œnanthic acid acts with acetate of copper in the same manner as with acetate of lead. — An alcoholic solution of œnanthic acid forms with an alcoholic solution of acetate of copper a precipitate which cakes together in boiling water, and becomes hard and friable when cold. Boiling alcohol extracts from it a salt which separates on cooling and contains 18·8 p. c. oxide of copper (sesquibasic salt) while a salt remains undissolved containing 28·4 p. c. oxide of copper, and therefore polybasic. (Liebig & Pelouze.)

An alcoholic solution of œnanthate of soda forms with acetate of copper a precipitate containing 12·3 per cent. of oxide of copper. (Mulder.)

*Œnanthate of Silver.* — Nitrate of silver is precipitated by œnanthate of soda (Liebig & Pelouze, Mulder), or œnanthate of ammonia (Delffs.)

| | | | | | | Liebig & Pelouze. | Mulder. | Delffs. |
|---|---|---|---|---|---|---|---|---|
| 32 C | 192 | 50·66 | 18 C | 108 | 40·75 | | 51·40 | 41·04 |
| 31 H | 31 | 8·18 | 17 H | 17 | 6·42 | | 8·09 | 6·51 |
| Ag | 108 | 28·49 | Ag | 108 | 40·75 | 35·67 | 27·14 | 40·49 |
| 6 O | 48 | 12·67 | 4 O | 32 | 12·08 | | 13·37 | 11·96 |
| $C^{32}H^{31}AgO^{6}$ | 379 | 100·00 | $C^{18}H^{17}AgO^{4}$ | 265 | 100·00 | | 100·00 | 100·00 |

Œnanthic acid dissolves readily in *alcohol* and *ether*.

## Œnanthic Ether.

AUBERGIER. (1821.) *Ann. Chim. Phys.* 14, 210.
LIEBIG & PELOUZE. *Ann. Pharm.* 19, 241.—*Ann. Chim. Phys.* 63, 113. —*Pogg.* 41, 571.—*Pharm. Centr.* 1837, 22.
MULDER. *Pogg.* 41, 582.—*Pharm. Centr.* 1837, 807.
STICKEL. *J. pr. Chem.* 9, 167.
CREUTZBURG. *J. pr Chem.* 10, 382.—*Pharm. Centr.* 1837, 574.
AUBERGIER, JUN. *J. Pharm.* 27, 286.
DELFFS. *Pogg.* 84, 505. — *Ann. Pharm.* 80, 290. — *Pharm. Centr.* 1852, 93.
LIEBIG. *Ann. Pharm.* 80, 290.

*Œnanthäther, Weinfuselöl, Huile de marc de raisin.*

This compound is the source of the odour of all wines and causes a single drop of wine in a bottle to be distinctly smelt, whereas aqueous alcohol has but a very faint odour; it must not however be confounded with the *bouquet*, which is different in different wines and absent altogether in many. (Liebig & Pelouze.)

*Formation and Preparation.* 1. When 5 pts. of sulphovinate of potash are heated with 1 pt. of œnanthic acid, the mixture fuses, and at 150° an oil rises to the surface, consisting of œnanthic ether and excess of œnanthic acid, which latter may be removed by heating with carbonate of potash. (Liebig & Pelouze.) — 2. This ether is also obtained in the preparation of French brandy from wine and wine-lees. The wine-lees are distilled with half their bulk of water; the resulting distillate, of 15° Cartier, is redistilled, whereby a distillate is obtained of 22° Cartier, and at last, when the distillate shows only 15°, œnanthic ether passes over with it; 10,000 pts. of this distillate yield only 1 pt. of œnanthic ether. (Liebig & Pelouze, according to Delechamps.) — The rough, sharp-tasting, colourless ether containing œnanthic acid (sometimes however coloured green by oxide of copper), is shaken up with aqueous carbonate of soda, and the milky mixture is heated to the boiling point; the œnanthic ether then rises to the surface and may be removed and dehydrated by chloride of calcium. (Liebig & Pelouze.) — 3. When the residues obtained in the distillation of *afterwine brandy* (*Weintrester-branntwein*) are again distilled, comparatively pure alcohol, becoming turbid when mixed with water, passes over at first, then alcohol containing fusel-oil, then a watery liquid rendered turbid by the presence of oil; the two latter liquids united, yield, when mixed with water, a considerable quantity of oil (150 litres

of brandy yield more than 32 grms.) In one preparation a crystalline unctuous mass was obtained. (Aubergier.) — 4. Fusel-oil obtained in the first distillation from fermented grain, and still retaining a greenish colour of oxide of copper after one rectification, is again rectified over aqueous carbonate of soda. The œnanthic ether thus obtained, still contains an oil not decomposible by potash, which also passes over in the decomposition of œnanthic ether by potash (*vid. inf.*); it has a very penetrating odour like that of *Phellandrium* and a sharp taste. (For its composition, vid. *Pogg*, 41, 582.) (Mulder.)

*Properties.* Transparent colourless oil, of sp. gr. 0·862, having a strong, intoxicating, vinous odour and a faint disagreeable taste. Boils between 225° and 230°. Vapour-density 9·8. (Liebig & Pelouze.) — Very mobile oil, colourless at first, but assuming a yellowish tint when exposed to light; has a very penetrating odour and sharp unpleasant taste. Less volatile than the volatile oils. (Aubergier.) — Fusel-oil obtained from the lees of Jena wine is light brown, viscid, and deposits a large quantity of stearoptene at 4°. Sp. gr. 0·856. Has a somewhat unpleasant odour like that of cheese from reindeer's milk, and an extremely nauseous taste, exciting violent irritation in the throat. Four drops make a sparrow uneasy, but produce no further symptoms. (Stickel.) — Fusel-oil from the lees of Austrian wine has a penetrating ethereal, vinous odour and a mild vinous taste; a few drops of it impart to pure alcohol the odour and taste of French brandy. It is less volatile than ether, more volatile than the volatile oils. (Creutzburg.) — Œnanthic ether obtained from a distillery in Kreuznach is yellowish and slightly acid, begins to boil at 240°, and exhibits a constant boiling point at 246°, one-fourth passing over between 246° and 250°. This portion, after being freed from a little acid by agitation with carbonate of soda, is colourless, and of sp. gr. 0·87 at 15°. Boiling point 224°, with the barometer at 27″ 8‴. Vapour-density=7·042. It has a pleasant vinous odour, and its taste is faint at first but afterwards produces irritation in the throat.

| I. | | | | II. | | | | Liebig & Pelouze. | Delffs. |
|---|---|---|---|---|---|---|---|---|---|
| 18 C | 108 | | 72·0 | 22 C | 132 | | 70·97 | 71·13 | 70·55 |
| 18 H | 18 | | 12·0 | 22 H | 22 | | 11·83 | 11·92 | 11·80 |
| 3 O | 24 | | 16·0 | 4 O | 32 | | 17·20 | 16·95 | 17·65 |
| $C^{18}H^{18}O^{3}$ | 150 | | 100·0 | $C^{22}H^{22}O^{4}$ | 188 | | 100·00 | 100·00 | 100·00 |

Calculation I is according to Liebig & Pelouze: II, according to Delffs (comp. page 362). Calculation II, gives the vapour-density 6·5 and boiling-point 207°. The formula I doubled corresponds to a vapour-density = 10·3993. [L.] [According to I, œnanthic ether should be composed of ½ vol. anhydrous acid and ½ vol. ether-vapour. J. L.]

*Decompositions.* 1. Œnanthic ether becomes yellowish when heated and leaves a yellowish residue by distillation. (Delffs.) — When distilled, it first passes over unaltered, and then yields a distillate having an empyreumatic odour; the residue in the retort becomes more and more yellow as the distillation goes on, and at last a very light charcoal remains. (Aubergier.) — 2. When kept for some time, it turns brown and acquires the power of reddening litmus; it burns with a yellowish red flame and leaves no residue. (Stickel.) — 3. Boiled with potash-ley,

it yields alcohol and œnanthate of potash. (Liebig & Pelouze, Mulder, Delffs.) — With alkalis it forms saponaceous compounds. (Aubergier.) — 4. It is not decomposed by alkaline carbonates or by ammonia, either in the form of gas or of aqueous solution. (Liebig & Pelouze.) — It does not dissolve in potash even after long boiling. (Stickel.) — 5. Heated with iodine, it emits a peculiar vinous odour. (Stickel.) — With chlorine it forms hydrochloric acid and chlorœnanthic ether. (Malaguti.)

Œnanthic ether is insoluble in water. — It imparts to water its taste and smell. (Aubergier.) — With ammonia it forms a liniment. (Stickel.)

It dissolves very readily in *alcohol*, even if very dilute; also in *ether*. (Liebig & Pelouze, Stickel.)

---

When the peels of 40 ripe quinces were distilled with water, a watery liquid passed over smelling strongly of quinces and having drops of oil floating upon it; more of these oily drops were obtained on distilling the water, but they altogether formed only one large drop. This oil has a very strong odour of quinces, and when distilled with potash-ley till the residue becomes inodorous, yields an oil having a similar odour; the inodorous potash-solution is rendered milky by sulphuric acid, and on heating it, an oil separates out which boils at about 10°, dissolves readily in potash, and is therefore probably œnanthic acid. (Wöhler, *Ann. Pharm.* 41, 239.)

## The so-called Anhydrous Œnanthic Acid.

LIEBIG & PELOUZE. *Ann. Pharm.* 19, 246.—*Pogg.* 41, 571.—*Pharm. Centr.* 1837, 24.
MULDER. *Pogg.* 41, 582.—*J. pr. Chem.* 12, 265.

In the distillation of œnanthic acid, water and œnanthic acid pass over first, but at last anhydrous œnanthic acid, which begins to boil at 260°; but the boiling point rises gradually to 294°, the liquid at the same time becoming coloured. After fusion it solidifies at 31°. Inodorous and tasteless. Reddens litmus. (Liebig & Pelouze.) According to Mulder, this compound is left when an alcoholic solution of œnanthic acid is left to evaporate slowly (p. 459).

| | | | Liebig & Pelouze. | Mulder. |
|---|---|---|---|---|
| 14 C | 84 | 74·33 | 73·63 | 73·22 |
| 13 H | 13 | 11·50 | 12·19 | 11·73 |
| 2 O | 16 | 14·17 | 14·18 | 15·05 |
| $C^{14}H^{13}O^{2}$ | 113 | 100·00 | 100·00 | 100·00 |

It absorbs 1 At. ammoniacal gas. (Mulder, Pelouze, *N. Ann. Chim. Phys.* 13, 259.)

## Chlorœnanthic Acid.

MALAGUTI. *Ann. Chim. Phys.* 70, 363.—*J. pr. Chem.* 18, 47.—*Pharm. Centr.* 1839, 580.

When chlorœnanthic ether is left in contact with potash-ley, till it is completely decomposed, then mixed with an acid, chlorœnanthic acid falls to the bottom in oily, slightly coloured drops. This oily liquid is saturated with carbonate of soda, the solution treated with animal charcoal, and precipitated by an acid, and the chlorœnanthic acid thus separated is washed with boiling water and dried in vacuo over oil of vitriol.

Colourless, very fluid, inodorous; has a disagreeable taste and reddens litmus.

| | | | Malaguti. |
|---|---|---|---|
| 14 C | 84·0 | 43·98 | 43·49 |
| 12 H | 12·0 | 6·28 | 6·43 |
| 2 Cl | 70·8 | 37·17 | 36·15 |
| 3 O | 24·0 | 12·57 | 13·93 |
| $C^{14}H^{12}Cl^2O^3$ | 190·8 | 100·00 | 100·00 |

From this composition it is impossible to deduce any formula in accordance with Delffs's view of œnanthic acid; $C^{15}H^{16}Cl^2O^4$ requires 47·58 p. c. C and 31·27 p. c. Cl, and $C^{18}H^{14}Cl^2O^4$ requires 41·30 p. c. C and 40·76 p. c. Cl. [L.]

The acid decomposes below the boiling point.

It combines with alkalis and heavy metallic oxides. The silver and copper salts decompose when washed with water.

## Chlorœnanthic Ether.

MALAGUTI. (1839.) *Ann. Chim. Phys.* 70, 363.—*J. pr. Chem.* 18, 47.—*Ann. Pharm.* 32, 35.—*Pharm. Centr.* 1839, 580.

*Ether œnanthique chloruré.*

Œnanthic ether in contact with chlorine gas becomes heated, gives off a large quantity of hydrochloric acid and turns yellow. When the liquid, after continued action, has regained its former temperature, it is decolorised by gentle heating, washed with potash-ley and then with water, and dried in vacuo over oil of vitriol.

Colourless syrup of sp. gr. 1·2912 at 16·5°, having a pleasant odour and a disagreeable bitter taste. Not volatile.

| I. | | | II. | | | Malaguti. |
|---|---|---|---|---|---|---|
| 18 C | 108·0 | 37·50 | 22 C | 36·82 | | 36·73 |
| 14 H | 14·0 | 4·86 | 17 H | 4·74 | | 5·30 |
| 4 Cl | 141·6 | 49·30 | 5 Cl | 49·51 | | 48·56 |
| 3 O | 24·0 | 8·34 | 4 O | 8·93 | | 9·41 |
| $C^{18}H^{14}Cl^4O^3$ | 287·6 | 100·00 | $C^{22}H^{17}Cl^5O^4$ | 100·00 | | 100·00 |

According to Malaguti's calculation I, chlorœnanthic ether = $C^4H^3Cl^2O,C^{14}H^{11}Cl^2O^2$ [or perhaps $2C^4H^3Cl^2O,C^{28}H^{22}Cl^4O^4$]. Calculation I corresponds to Delffs's view of œnanthic acid.

Chlorœnanthic ether blackens at a strong heat and gives off hydrochloric acid gas, a heterogeneous liquid then distilling over, whose boiling point rises as the distillation goes on; in the retort there remains a very acid pitch-like mass. The ether is slowly decomposed by potash-ley, but completely after some days; the liquid contains hydrochlorate and acetate of potash and acids separate œnanthic acid from it.

It dissolves in 15 or 16 pts. of alcohol at 40°.

## ¶. Chloride of Œnanthylene. $C^{14}H^{14},Cl^2$

LIMPRICHT. *Ann. Pharm.* 103, 80.

*Formation.* By the action of pentachloride of phosphorus on œnanthol.

*Preparation.* When 1 At. œnanthol is gradually allowed to flow into 1 At. pentachloride of phosphorus contained in a tubulated retort, great heat is evolved, and a portion of the resulting chlorophosphoric acid distils over immediately. As soon as the decomposition of the pentachloride is complete, the liquid is subjected to fractional distillation, the portion which boils above 150° being collected apart as long as it passes over colourless; in the retort there remains a small quantity of a brown thick liquid. The last distillate is washed with water to remove adhering chlorophosphoric acid; and the oil which floats on the water is shaken up with bisulphite of soda to remove undecomposed œnanthol, then dried with chloride of calcium and rectified, the portion which boils between 180° and 200° being collected apart; on again rectifying this portion, pure chloride of œnanthylene passes over at 187°.

*Properties.* Transparent, colourless, mobile liquid, lighter than water, having a not unpleasant odour, like that of œnanthol. It boils at 191°. (The boiling point read off was 187°, but a correction of 4° is made for the column of mercury not immersed in the liquid.)

| | | | Limpricht. |
|---|---|---|---|
| 14 C | 84·0 | 49·4 | 48·85 |
| 14 H | 14·0 | 8·2 | 8·0 |
| 2 Cl | 70·8 | 42·4 | 42·5 |
| $C^{14}H^{14}Cl^2$ | 168·8 | 100·0 | 98·90 |

The compound gently heated with sodium is decomposed with violence, yielding œnanthylene and chloride of sodium. — Boiled for some time with ethylate of sodium or alcoholic solution of potash, it is resolved into hydrochloric acid, chlorœnanthylene $C^{14}H^{13}Cl$, and a hydrocarbon, probably $C^{14}H^{12}$:

$$C^{14}H^{14}Cl^2 - 2HCl = C^{14}H^{12}.$$

It is not perceptibly decomposed by acetate of silver, even when continuously boiled with it or heated to 250° in sealed tubes. (Limpricht.) ¶

*Oxygen-nucleus* $C^{14}H^{13}O$.

## Anhydrous Œnanthylic Acid.

$C^{14}H^{13}O^3 = C^{14}H^{13}O,O^2$.

CHIOZZA & MALERBA. (1854.) *Ann. Pharm.* 91, 102.—*J. pr. Chem.* 64, 32.—*Pharm. Centr.* 1854, 739.

*Œnanthylic Anhydride, Œnanthylic Œnanthylate.*

*Preparation.* By mixing 6 At. of perfectly dry œnanthylate of potash with 1 At. chlorophosphoric acid. The action begins spontaneously, giving rise to evolution of heat, and it is merely necessary to heat the mixture slightly just at the last. In other respects the process is conducted as in the preparation of anhydrous benzoic acid (p. 94). Œnanthylate of baryta is not so easily attacked as the potash-salt.

*Properties.* Colourless oil, of sp. gr. 0·91 at 14°. At ordinary temperatures, it has a faint odour somewhat like that of anhydrous caprylic acid; when heated it gives off an aromatic odour; if kept in badly closed vessels, it smells rancid.

| | | | Malerba. |
|---|---|---|---|
| 14 C | 84 | 69·42 | 69·20 |
| 13 H | 13 | 10·74 | 10·51 |
| 3 O | 24 | 19·84 | 20·29 |
| $C^{14}H^{13}O^3$ | 121 | 100·00 | 100·00 |

With alkalis, it behaves like other anhydrides. With caustic ammonia it forms œnanthylamide.

## Benzoic Œnanthylate.

$C^{28}H^{18}O^6 = C^{14}H^5O^2,C^{14}H^{13}O^3$.

CHIOZZA & MALERBA. *loc. cit.*

Produced by the action of chloride of benzoyl on œnanthylate of potash.

Colourless oil of sp. gr. 1·043. Smells like œnanthylic anhydride. When recently prepared, it has no action on litmus paper.

| | | | Malerba. |
|---|---|---|---|
| 28 C | 168 | 71·79 | 71·85 |
| 18 H | 18 | 7·69 | 7·58 |
| 6 O | 48 | 20·52 | 20·57 |
| $C^{28}H^{18}O^6$ | 234 | 100·00 | 100·00 |

In contact with the air, it quickly becomes filled with crystals of benzoic acid.

*Oxygen-nucleus* $C^{14}H^{12}O^2$.

## Pimelic Acid.

$C^{14}H^{12}O^8 = C^{14}H^{12}O^2,O^6$.

LAURENT. (1837.) *Ann. Chim. Phys.* 66, 163.—*J. pr. Chem.* 27, 316. —*Pharm. Centr.* 1838, 280.
BROMEIS. *Ann. Pharm.* 35, 104.—*Pharm. Centr.* 1840, 615.
RADCLIFF. *Ann. Pharm.* 43, 353.—*Pharm. Centr.* 1842, 907.
GERHARDT. *Rev. scient.* 19, 13.
SACC. *Ann. Pharm.* 51, 221.—*Pharm. Centr.* 1844, 876.
MARSH. *Ann. Pharm.* 104, 121.

*Pimelinic acid, Pimelinsäure.*

*Formation.* By the action of nitric acid on caprylic alcohol (Bouis), oleic acid, linseed-oil, wax or spermaceti. — Also, according to Sacc, when a mixture of pure succinic acid and excess of suberic acid is heated with nitric acid [? L.]

$$2C^8H^6O^8 + C^{16}H^{14}O^8 + 2O = 2C^{14}H^{12}O^8 + 4CO^2 + 2HO.$$

*Preparation.* 1. The hard crystalline grains of pimelic acid contaminated with suberic acid which are obtained in the preparation of lipic acid (x, 434), are freed from adhering suberic acid by elutriation with water and washing with cold alcohol, and recrystallised from boiling water. (Laurent.) — According to Bromeis, pimelic acid occurs, not so much in the acid mother-liquor of suberic acid prepared by Laurent's method, as in the wash-water; and crystallises therefrom by slow evaporation. It is purified by repeated crystallisation from boiling water. — Marsh separates the suberic acid as completely as possible by repeated crystallisation; concentrates the mother-liquor very strongly; presses the separated mixture of acids between bibulous paper; dissolves them in water; mixes the warm solution with a quantity of strong aqueous carbonate of soda sufficient to impart a slight alkaline reaction; treats the concentrated liquid with chloride of barium as long as suberate of baryta is thereby precipitated; and mixes the liquid decanted from the precipitate after cooling with a warm concentrated solution of sulphate of copper. The precipitation must not be performed at too high a temperature, otherwise the pimelate of copper as it separates, will partially fuse and cake together. The light blue precipitate of pimelate of copper is suspended in water and decomposed with sulphuretted hydrogen, and the liquid is evaporated to the crystallising point, the first portions, which possibly still contain a little suberic acid, being set aside, and the last portions being regarded as pure pimelic acid. — Sacc, in preparing suberic acid by the oxidation of linseed-oil with nitric acid, obtained from the mother-liquor containing nitric acid which was left after the first crystallisation of suberic acid, — first, fresh quantities of suberic acid, and then larger granules or hard yellowish plates of pimelic acid, which were purified by distillation. — 2. When 1 pt. of wax is boiled with 2 pts. of nitric acid till the whole is dissolved, granules of pimelic acid separate first as the liquid cools. (Gerhardt.) — 3. Radcliffe digested spermaceti with moderately strong

nitric acid till the whole was dissolved; the solution when evaporated and left to cool, yielded, besides succinic acid, white granules of pimelic acid. If the digestion be continued, the pimelic acid diminishes in quantity and the succinic acid increases, so that it is only the mother-liquor of the succinic acid that then yields pimelic acid. — In another experiment, Radcliff obtained an acid which separated in transparent crystals, arranged in groups like cauliflower-heads; this acid dissolved readily in water and exhibited the composition of adipic acid. — 4. When a mixture of succinic and excess of suberic acid is boiled with strong nitric acid, and the excess of suberic acid is removed by evaporation and cooling, the mother-liquor yields very beautiful pimelic acid without any trace of succinic or suberic acid. (Sacc.) [! L.]

*Properties.* White granules of the size of pins' heads and composed of small crystals. (Laurent.) Needle-shaped crystals grouped in hard, warty, stellate masses. (Marsh.) Has no smell, but a sour taste. (Laurent.) Tastes sour, somewhat like tartaric acid. (Marsh.) Melts at 114° (Laurent); at 134° (after drying at 100°). (Bromeis.) When perfectly dry, it softens at 112° and melts at 114° or 115° (a specimen imperfectly dried melted at 90°), and solidifies on cooling, into a brittle mass of needle-shaped crystals. (Marsh.) Distils without decomposition at a high temperature. (Laurent.) Boils at a high temperature apparently between 230° and 235°, turning slightly brown, and distilling in the form of a transparent oil which forms needle-shaped crystals on cooling. (Marsh.)

| | *At* 100°. | | | Laurent. | Bromeis. | Radcliff. | Gerhardt. |
|---|---|---|---|---|---|---|---|
| 14 C | 84 | 52·50 | | 51·78 | 51·75 | 51·08 | 52·0 |
| 12 H | 12 | 7·50 | | 7·55 | 7·55 | 7·52 | 7·8 |
| 8 O | 64 | 40·00 | | 40·67 | 40·70 | 41·40 | 40·2 |
| $C^{14}H^{12}O^{8}$ | 160 | 100·00 | | 100·00 | 100·00 | 100·00 | 100·0 |

*Decompositions.* When fused with hydrate of potash, it gives off a large quantity of water, and at a stronger heat, hydrogen gas: the residue turns yellow, contains oxalic acid, and when distilled with sulphuric acid, yields a volatile acid having the odour of valerianic acid, and forming a silver-salt which blackens quickly when exposed to light. (Gerhardt):

$$C^{14}H^{12}O^{8} + 4HO = C^{4}H^{2}O^{8} + C^{10}H^{10}O^{4} + 4H.$$

*Combinations.* Pimelic acid dissolves in 35 pts. of water at 18°, very easily in boiling water. (Laurent.) It is more soluble in water than suberic acid. (Bromeis.) It dissolves in heated oil of vitriol. (Laurent.)

*Pimelates.* — The acid is bibasic. Only its neutral salts, $C^{14}H^{10}M^{2}O^{8}$, are known. Nevertheless, a solution of pimelic acid boiled with the recently precipitated carbonates of baryta, strontia, lime or magnesia, even for a considerable time, does not dissolve a sufficient quantity of the bases to form neutral salts.

*Pimelate of Ammonia* dissolved in water gives off ammonia when boiled, and when left to itself for some time, especially in a warm place. (Marsh.)

*Pimelate of Baryta.* — Obtained by boiling the aqueous acid with carbonate of baryta. (Laurent.)

| | | | Laurent. |
|---|---|---|---|
| 2 BaO | 153·2 | 51·39 | 51·07 |
| $C^{14}H^{10}O^6$ | 142·0 | 48·61 | |
| $C^{10}H^{10}Ba^2O^8$ | 295·2 | 100·00 | |

The acid neutralised with ammonia does not precipitate the salts of *baryta, strontia, lime* or *magnesia* (Laurent, Bromeis, Marsh), or *manganous* oxide or *zinc*-oxide. (Laurent, Bromeis.) — With zinc-salts it forms a white bulky precipitate, which, if sulphuric acid is present, appears only when the liquid is heated. (Marsh.) — With *lead*-salts a white precipitate (Laurent), apparently insoluble in water and alcohol. (Marsh.) With *ferric* salts a light red precipitate. With *mercuric* chloride a white precipitate. (Laurent.)

*Pimelate of Copper.* — The ammonia-salt forms with cupric salts a green precipitate (Laurent); a blue precipitate insoluble in water and alcohol. With acetate of copper however no precipitate is formed, the mixture of the two salts leaving only a syrupy mass when evaporated. (Marsh.)

| | | | Marsh. | |
|---|---|---|---|---|
| 2 CuO | 79·6 | 35·86 | 35·2 | 34·25 |
| $C^{14}H^{10}O^6$ | 142·0 | 64·14 | | |
| $C^{14}H^{10}Cu^2O^8$ | 221·6 | | | |

*Pimelate of Silver.* — The neutral ammonia-salt forms a white precipitate with nitrate of silver.

| | | | Bromeis. | Radcliff. | Marsh. |
|---|---|---|---|---|---|
| 14 C | 84 | 22·46 | 22·19 | 23·37 | |
| 10 H | 10 | 2·67 | 2·64 | 2·89 | |
| 2 AgO | 232 | 62·04 | 62·19 | 60·00 | 61·15 |
| 6 O | 48 | 12·83 | 12·92 | 13·74 | |
| $C^{14}H^{10}Ag^2O^8$ | 374 | 100·00 | 100·00 | 100·00 | |

Pimelic acid dissolves readily in warm *alcohol* and *ether*.

## ¶. Pimelate of Ethyl.

$$C^{22}H^{20}O^8 = 2C^4H^5O,C^{14}H^{10}O^6.$$

MARSH. *Ann. Pharm.* 104, 125.

Obtained by the repeated action of hydrochloric acid on an alcoholic solution of pimelic acid. The portion which is volatile below 100° is distilled off; the residue neutralised with carbonate of soda; and the dark red oil thereby separated — the quantity of which increases on further addition of water — is dehydrated by means of chloride of calcium. — The liquid thus obtained has an agreeable fruity odour and the following composition :

| | | | | | Marsh. |
|---|---|---|---|---|---|
| 22 C | 132 | .... | 61·11 | ..... | 61·44 |
| 20 H | 20 | .... | 9·25 | ..... | 9·76 |
| 8 O | 64 | .... | 29·64 | ..... | 28·80 |
| $C^{22}H^{20}O^{8}$ | 216 | .... | 100·00 | ..... | 100·00 |

It begins to boil at 185°, but the boiling point gradually rises, charcoal separates, and a liquid passes over which effervesces with carbonate of soda, and appears to be *Ethylopimelic acid*, $C^{4}H^{5}O,HO,C^{14}H^{10}O^{6}$. Its composition is:

| *Dried over chloride of calcium.* | | | | | Marsh. |
|---|---|---|---|---|---|
| 18 C | 144 | .... | 57·44 | ..... | 57·03 |
| 16 H | 16 | .... | 8·50 | ..... | 9·10 |
| 8 O | 64 | .... | 34·06 | ..... | 33·87 |
| $C^{18}H^{16}O^{8}$ | 324 | .... | 100·00 | ..... | 100·00 |

*Pimelate of Methyl.* — $2C^{2}H^{3}O,C^{14}H^{10}O^{6}$, is prepared in a similar manner to the ethyl-compound, and undergoes the same kind of decomposition when boiled.

## ¶. Pimelate of Amyl.

$C^{34}H^{32}O^{8} = 2C^{10}H^{11}O,C^{14}H^{10}O^{6}$.

MARSH. *Ann. Pharm.* 104, 124.

Hydrochloric acid gas is passed into a solution of pimelic acid in amylic alcohol; the portion which boils below 130°, distilled off; the residue mixed with a fresh portion of amylic alcohol; hydrochloric acid again passed into the liquid; and the portion volatile below 130° again distilled off. The dark red residue begins to boil at 260°, but the boiling point soon rises to 280°, and a dark red oily liquid passes over. Lastly, this liquid, together with that which is extracted by alcohol from the blackened residue in the retort, is rectified, the portion which distils below 150° being rejected, and that obtained between 170° and 200°, collected apart.

Dark red somewhat oily liquid, having a penetrating but not unpleasant odour.

| | | | | | Marsh. |
|---|---|---|---|---|---|
| 34 C | 204 | .... | 68·00 | ..... | 67·64 |
| 32 H | 32 | .... | 10·67 | ..... | 10·90 |
| 8 O | 64 | .... | 21·33 | ..... | 21·46 |
| $C^{34}H^{32}O^{8}$ | 300 | .... | 100·00 | ..... | 100·00 |

Insoluble in water, soluble in *alcohol* and *ether*. ¶

*Oxygen-nucleus* $C^{14}H^{10}O^4$.

## Terebilic Acid.

$C^{14}H^{10}O^8 = C^{14}H^{10}O^4,O^4$.

BROMEIS. (1841.) *Ann. Pharm.* 37, 297.—*Pharm. Centr.* 1841, 399.
RABOURDIN. *N. J. Pharm.* 6, 185.—*Pharm. Centr.* 1845, 213.
CAILLOT. *L'Inst.* 1849, 353.—*N. Phil. Mag.* 36, 67.

*Terebic acid, Terebilsäure, Terebinsäure, Terpenthinsäure* (Bromeis), *Acide térébique, Acide térébilique* (Rabourdin).

*Formation.* By the action of strong nitric acid on oil of turpentine or colophonium.

*Preparation.* When oil of turpentine or colophonium is boiled with nitric acid, a violent action takes place. When oil of turpentine is used, the mixture is thrown out of the vessel; colophonium acts more quietly, and after a few days, the whole dissolves, forming a clear liquid, which when mixed with water becomes turbid and deposits resin. After evaporating to dryness, and treating the residue with water, nothing remains but a small quantity of resin; and the acid solution, which is almost free from nitric acid yields by evaporation a yellowish syrup which, if left for some time in the cold, deposits crystals of terebilic acid; they may be washed with water and dried between paper. (Bromeis.) — When a small quantity of oil of turpentine (obtained from *Pinus maritima*), is heated with commercial nitric acid, a very violent action takes place at 60°; and if more oil of turpentine be added in successive portions, the nitric acid being however kept in excess, and the liquid being ultimately boiled, till the resin which separates at first is completely dissolved, a saffron-coloured resin is precipitated on addition of water, and the liquid after being evaporated to a syrup, yields crystals of oxalic acid. The mother-liquor diluted with water in order to precipitate a small remaining quantity of resin, and then again evaporated to a syrup, yields terebilic acid in a few days in the form of a granular mass; (if no such product is obtained, the syrup must be mixed with an equal volume of nitric acid and evaporated over the water-bath to its former bulk). The granular crystals are washed with cold water and recrystallised twice or three times. (Rabourdin.)

*Properties.* Four-sided prisms with oblique terminal faces, and having a strong lustre on the lateral faces. (Bromeis.) Crystallises from the alcoholic solution by spontaneous evaporation in transparent colourless rectangular prisms and acute or wedge-shaped octohedrons; from the aqueous solution, on cooling, in small crystals united in groups like cauliflower-heads. (Rabourdin.) Melts with some difficulty (Bromeis); at 200°, without loss of weight (Rabourdin); fumes slightly when strongly heated, but does not sublime. (Bromeis, Rabourdin.) Its taste is purely acid. (Rabourdin.)

| | At 100°. | | | Bromeis. | Rabourdin. |
|---|---|---|---|---|---|
| 14 C | 84 | 53·16 | | 53·20 | 53·03 |
| 10 H | 10 | 6·33 | | 6·76 | 6·43 |
| 8 O | 64 | 40·51 | | 40·04 | 40·54 |
| $C^{14}H^{10}O^{8}$ | 158 | 100·00 | | 100·00 | 100·00 |

The behaviour under the influence of heat makes it doubtful whether the acid examined by Bromeis was the same as that examined by Rabourdin.

*Decompositions.* 1. The acid when heated, decomposes with slight ntumescence. (Bromeis.) When heated to the boiling point, it gives off arbonic acid and yields a distillate of pyroterebilic acid, without leaving any residue in the retort. (Rabourdin.)

2. It is not altered by boiling with nitric acid, but oil of vitriol blackens it. (Rabourdin.)

3. According to Caillot's researches, which are known only in abstract, terebilic acid, in presence of excess of bases, takes up 2 or 3 At. water and forms two new acids; with lime, cupric oxide, lead-oxide and silver-oxide, *diaterebates* are formed, = $C^{14}H^{10}O^{8},2MO$; with potash, soda, baryta, strontia, magnesia and magnanous oxide, *metaterebates* = $C^{14}H^{11}H^{8},2MO$. When hydrated oxide of lead is dissolved in terebilic acid or terebilate of lead (obtained by dissolving carbonate of lead in the aqueous acid) the salt $C^{14}H^{8}O^{7},5PbO$ is formed, which dissolves in water in all proportions and when boiled yields $C^{14}H^{8}O^{8},7PbO$.

*Combinations.* Terebilic acid dissolves sparingly in cold water, but is much more soluble in boiling water. (Rabourdin.)

The *Terebilates* are soluble in water, the ferric salt only being difficult to dissolve; the terebilates of the alkalis and earths dissolve very easily and crystallise with difficulty. (Rabourdin.) The ammoniacal solution does not precipitate a solution of chloride of calcium, acetate of lead or nitrate of silver. (Bromeis.)

*Terebilate of Lead.* — *a. Basic.* — The aqueous solution of *b* dissolves a large quantity of oxide of lead, forming a basic salt which crystallises with difficulty. The aqueous solution does not precipitate basic acetate of lead.

*b. Neutral.* — When oxide of lead is dissolved in the aqueous acid in such quantity as to leave the liquid still acid, and the solution is then evaporated to a syrup at a gentle heat, white crusts form on cooling, consisting of crystals aggregated in cauliflower-like groups. Dissolves readily in water. (Rabourdin.)

*Ferric* salts are precipitated by alkaline terebilates; in dilute solutions a blood-red colour is produced. (Rabourdin.)

*Terebilate of Silver.* — A strong aqueous solution of nitrate of silver is precipitated by an alkaline terebilate in slight excess; and the precipitate is washed with a little cold water, pressed between paper and dried by heat in a dark place. Four-sided needles having a strong lustre. It blackens when exposed to light, especially if moist. (Rabourdin.) Bromeis, by mixing terebilate of ammonia with a slight excess of nitrate of silver and evaporating, obtained, as the liquid cooled, needles grouped in tufts and having a fine silky lustre; they decomposed at a rather high temperature, and when slowly heated, left silver in the form of the crystals.

| | At 100°. | | Rabourdin. | Bromeis. |
|---|---|---|---|---|
| 14 C | 84 | 31·70 | 31·61 | |
| 9 H | 9 | 3·40 | 3·44 | |
| AgO | 116 | 43·77 | 43·89 | 44·22 |
| 7 O | 56 | 21·13 | 21·06 | |
| $C^{14}H^{9}AgO^{8}$ | 265 | 100·00 | 100·00 | |

Terebilic acid dissolves very readily in *alcohol* and in *ether*.

*Terebilate of Methyl.* $C^{16}H^{12}O^{8} = C^{2}H^{3}O,C^{14}H^{9}O^{7}$. — Oil having a burning, but not acid taste. Cannot be distilled without decomposition. — Dissolves sparingly in water. With bases it forms salts having but little stability. (Caillot, *L'Institut*. 1849, 354.)

*Terebilate of Ethyl.* $C^{18}H^{14}O^{8} = C^{4}H^{5}O,C^{14}H^{9}O^{7}$. — Oil, having a burning but not acid taste. — Cannot be distilled without decomposition. — Sparingly soluble in water. With bases, it forms salts which have but little stability and are resolved by the slightest heat into metaterebates, alcohol and terebate of ethyl: *e g.*

$$2(C^{14}H^{8}O^{6},BaO,C^{4}H^{5}O) + 7HO = C^{14}H^{12}O^{11},2BaO + C^{4}H^{6}O^{2} + C^{14}H^{9}O^{7},C^{4}H^{5}O.$$

(Caillot; see page. 468).

*Terebilate of Amyl.* $C^{24}H^{20}O^{8} = C^{10}H^{11}O,C^{14}H^{9}O^{7}$. — Resembles the ethyl-compound. (Caillot.)

*Chlorine-nucleus* $C^{14}ClH^{13}$.

## ¶. Chlorœnanthylene. $C^{14}ClH^{13}$.

LIMPRICHT. *Ann. Pharm.* 103, 82.

*Formation.*—By the action of alcoholic potash or ethylate of sodium on chloride of œnanthylene (p. 461).

*Preparation.* A very concentrated alcoholic solution of potash is distilled upwards with chloride of œnanthylene for a considerable time (the decomposition of 15 grammes of the chloride takes about a week); — or chloride of œnanthylene and ethylate of sodium are heated together in a sealed tube to 250°; — the liquid obtained by either process is diluted with water which separates impure chlorœnanthylene; and this crude product is dried by means of chloride of calcium and then subjected to fractional distillation. It begins to boil at 100°, the boiling point slowly rising to 150°, where it remains constant for a while and ultimately rises to 190°. The liquid which passes over below 100° is a hydrocarbon (*vid. inf.*); that which distils at 152° is chlorœnanthylene, and above that temperature the product consists chiefly of undecomposed chloride of œnanthylene. The complete separation of these liquids can be effected only by repeated rectification.

*Properties.* Liquid resembling chloride of œnanthylene and having a similar odour. Boils at 155° (observed boiling point 152°; correction 3°).

| | | | Limpricht. |
|---|---|---|---|
| 14 C | 84·0 | 63·2 | 63·5 |
| 13 H | 13·0 | 9·7 | 9·7 |
| Cl | 35·4 | 27·1 | 26·8 |
| $C^{14}ClH^{13}$ | 132·4 | 100·0 | 100·0 |

Sodium remains unaltered in chlorœnanthylene at ordinary temperatures; but on heating the liquid, a violent action suddenly takes place, chloride of sodium being formed together with a hydrocarbon, probably $C^{14}H^{12}$. — The same hydrocarbon appears to be produced by the action of alcoholic potash on chlorœnanthylene; for the portion of the liquid obtained in the preparation of chlorœnanthylene above described, which boiled below 100°, was found to contain 84·14 p. c. carbon and 12·42 hydrogen, besides a certain quantity of chlorine. Supposing now that the deficient 3·4 per cent. consisted of chlorine, arising from an admixture of chlorœnanthylene with the hydrocarbon, and deducting from the preceding quantities of carbon and hydrogen the quantities of those elements corresponding to this 3·4 p. c. of chlorine, there remains 76·3 C and 11·2 H, or 87·5 p. c. C and 12·5 H, agreeing very nearly with the formula $C^{14}H^{12}$, which requires 87·2 p. c. C and 12·8 H. The analysis of another specimen calculated in a similar manner gave 87·7 p. c. and 12·3 H. The formation of this hydrocarbon from chloride of œnanthylene and from chlorœnanthylene is represented by the equations: $C^{14}H^{14}Cl^2 - 2HCl = C^{14}H^{12}$; and $C^{14}H^{13}Cl - HCl = C^{14}H^{12}$. (Limpricht.) ¶.

## Chloride of Œnanthyl.

$C^{14}ClH^{13}O^2 = C^{14}ClH^{13},O^2$ [$= C^{14}H^{13}O^2,Cl$].

CAHOURS. *Compt. rend.* 25, 724.

Produced by distilling œnanthylic acid with pentachloride of phosphorus.

It is decomposed by water into hydrochloric and œnanthylic acids.

### *Chlorine-nucleus* $C^{14}Cl^3H^{11}$.

## Terchlorœnanthol.

$C^{14}Cl^3H^{11}O^2 = C^{14}Cl^3H^{11},O^2$.

WILLIAMSON. (1847.) *Ann. Pharm.* 61, 44.

Œnanthol absorbs a large quantity of chlorine gas, and is converted, with formation of hydrochloric acid, into a viscid oil, which is washed with water and freed from hydrochloric acid by repeated solution in alcohol and precipitation by water. — It has an agreeable odour, something like that of caoutchouc. It sinks in water, but does not appear to be decomposed by it, even after long immersion. It cannot be distilled without decomposition.

| | | | Williamson. |
|---|---|---|---|
| 14 C | 84·0 | 38·62 | 38·1 |
| 11 H | 11·0 | 5·06 | 5·2 |
| 3 Cl | 106·2 | 48·96 | |
| 2 O | 16·0 | 7·36 | |
| $C^{14}H^{11}Cl^3O^2$ | 217·2 | 100·00 | |

When heated, it blackens and gives off hydrochloric acid.

*Amidogen-nucleus* $C^{14}AdH^{13}$.

## Œnanthylamide.

$C^{14}NH^{15}O^2 = C^{14}AdH^{13},O^2$.

CHIOZZA & MALERBA. (1854.) *Ann. Pharm.* 91, 103.—*J. pr. Chem.* 64, 32.

Œnanthylic anhydride forms with strong caustic ammonia a mass of small crystals which may be recrystallised from boiling water. — Laminæ having a pearly lustre. Melts at 95° and volatilises without decomposition at a higher temperature.

| | | | Malerba. |
|---|---|---|---|
| 14 C | 84 | 65·12 | 65·32 |
| N | 14 | 10·85 | |
| 15 H | 15 | 11·63 | 11·65 |
| 2 O | 16 | 12·40 | |
| $C^{14}NH^{15}O^2$ | 129 | 100·00 | |

*Oxyazo-nucleus* $C^{14}N^4H^6O^4$.

## Theobromine.

$C^{14}N^4H^6O^4 = C^{14}N^4H^6O^4,H^2$. ?

WOSKRESENSKY. (1841.) *Ann. Pharm.* 41, 125. — *J. pr. Chem.* 23, 394.—*Pharm. Centr.* 1841, 520.
BLEY. *N. Br. Arch.* 29, 201.—*Pharm. Centr.* 1842, 303; 1846, 424.
KELLER. *Ann. Pharm.* 92, 71.—*J. pr. Chem.* 64, 190.—*Pharm. Centr.* 64, 190.—*Pharm. Centr.* 1855, 95.

*Sources.* In cacao-beans (Woskresensky), and in small quantity in their husks. (Bley.)

*Preparation.* Cacao-beans are treated with water for some time at the heat of the water-bath; the solution is strained through linen, and carefully precipitated by neutral acetate of lead; the precipitate, which is abundant, is separated by filtration; and the filtered liquid is freed from excess of lead by sulphuretted hydrogen. The filtrate then yields by evaporation a brown residue, which is boiled with alcohol and filtered at the boiling heat; the liquid on cooling deposits a reddish white crystalline powder, which is obtained colourless by repeated crystallisation. (Woskresensky, Glasson.) Keller heats the theobromine obtained as above, between two watch-glasses, whereby a small quantity of charcoal is separated, and a dazzling white sublimate is formed.

*Properties.* Colourless crystalline powder. Microscopic crystals belonging to the right prismatic system: $\infty P2$; P in club-shaped groups.

(Keller.) Tastes very bitter, but the flavour is very slowly developed. (Woskresensky, Glasson.) Sublimes without decomposition between 290° and 295°. (Keller.)

| | | | Woskresensky. | Glasson. | Keller. |
|---|---|---|---|---|---|
| 14 C | 84 | 46·67 | 46·33 | 47·13 | 46·28 |
| 4 N | 56 | 31·11 | 35·38 | 31·27 | 30·86 |
| 8 H | 8 | 4·44 | 4·55 | 4·60 | 4·80 |
| 4 O | 32 | 17·78 | 13·74 | 17·00 | 18·06 |
| $C^{14}N^4H^8O^4$ | 180 | 100·00 | 100·00 | 100·00 | 100·00 |

*Decompositions.* 1. With chlorine in presence of water, it forms amalic acid (xi, 433) and hydrochlorate of methylamine. (Rochleder & Hlasiwetz, *Wien. Akad.* 1850, 1, 266.) — 2. Heated with peroxide of lead and dilute sulphuric acid, it gives off carbonic acid, the decomposition when once begun, going on without further application of heat; and if the right quantity of peroxide of lead be added and the heating not too long continued, there is obtained, after separating the sulphate of lead by filtration, a transparent colourless liquid, which gives off ammonia when treated with potash, separates sulphur from sulphuretted hydrogen, colours the skin purple-red, and immediately turns blue when treated with magnesia. An excess of magnesia destroys this colour, which may however be restored by cautious addition of sulphuric acid. The liquid mixed with excess of magnesia, becomes reddish and gives off ammonia during evaporation to dryness; boiling alcohol extracts from the residue a body which crystallises from the solution in rhombic prisms, is soluble in alcohol, has an acid reaction, and does not precipitate chloride of mercury, nitrate of silver or bichloride of platinum. (Glasson.)

3. It dissolves in boiling baryta-water without evolution of ammonia; the solution on cooling, solidifies into a white jelly.

*Combinations.* Theobromine is sparingly soluble in hot water. With acids it forms salts which crystallise readily. The neutral salts are decomposed by water and yield basic salts.

*Hydrochlorate of Theobromine.* — Theobromine dissolves readily in concentrated hydrochloric acid; as the warm solution cools, the salt separates in crystals, which may be dried over oil of vitriol and caustic potash. Gives off all its hydrochloric acid at 100°. Decomposes with water forming a basic salt. (Glasson.)

| | | | Glasson. |
|---|---|---|---|
| $C^{14}N^4H^8O^4$ | 180·0 | 83·17 | |
| ClH | 36·4 | 16·83 | 16·83 |
| $C^{14}N^4H^8O^4$,ClH | 216·4 | 100·00 | |

*Nitrate of Theobromine.* — A solution of theobromine in slightly heated nitric acid deposits the nitrate after a while, on cooling, in oblique rhombic prisms. The salt gives off its acid at 100°, and is readily decomposed by water.

| | | | Glasson. |
|---|---|---|---|
| $C^{14}N^4H^8O^4$,HO | 189 | 77·78 | |
| $NO^5$ | 54 | 22·22 | 22·87 |
| $C^{14}N^4H^8O^4$,$NO^5H$ | 243 | 100·00 | |

*Nitrate of Silver and Theobromine.* — A very dilute aqueous solution of nitrate of theobromine mixed with nitrate of silver forms after a short time, silver-white needles. The double salt is but sparingly soluble in water, and may therefore serve as a test for theobromine. It does not suffer any perceptible loss at 100°, but at a higher temperature it melts, gives off red fumes, and after continued ignition in contact with the air, leaves a residue of metallic silver. (Glasson.)

| | | | | Glasson. |
|---|---|---|---|---|
| 14 C | 84 | .... | 24·00 | 23·71 |
| 5 N | 70 | .... | 20·00 | 19·76 |
| 8 H | 8 | .... | 2·28 | 2·47 |
| 9 O | 72 | .... | 20·58 | 21·22 |
| AgO | 116 | .... | 33·14 | 32·84 |
| $C^{14}N^4H^8O^4,NO^6 + AgNO^6$ | 350 | .... | 100·00 | 100·00 |

*Chloroplatinate of Theobromine.* — A mixture of theobromine dissolved in hydrochloric acid with bichloride of platinum, yields prisms belonging to the oblique prismatic system, and having the faces ∞P an 0P. The salt effloresces in the air, and gives off all its water of crystallisation (8·73 p. c. = 4 At.) at 100°. It decomposes at a stronger heat, and when ignited in the air leaves pure platinum.

| | | | | Glasson. | Keller. |
|---|---|---|---|---|---|
| $C^{14}N^4H^8O^4,HCl$ | 216·4 | .... | 56·03 | | |
| 2 Cl | 70·8 | .... | 18·33 | | |
| Pt | 99·0 | .... | 25·64 | 25·42 | 25·55 |
| $C^{14}N^4H^8O^4,HCl + PtCl^2$ | 386·2 | .... | 100·00 | | |

Aqueous theobromine forms with a solution of corrosive sublimate, a white crystalline precipitate, sparingly soluble in water and alcohol. (Woskresensky.)

Theobromine is less soluble in alcohol and ether even than in water. It forms with tannic acid a precipitate soluble in excess of the acid, in hot water and in alcohol.

*Primary-nucleus* $C^{14}H^{16}$.

*Oxygen-nucleus* $C^{14}H^{10}O^6$.

## Boheic Acid.

$C^{14}H^{10}O^{12} = C^{14}H^{10}O^6,O^6$.

ROCHLEDER. (1847.) *Ann. Pharm.* 63, 202.—*Pharm. Centr.* 1848, 25.

Occurs in small quantity in black tea, together with a large quantity of quercitannic acid.

*Preparation.* A decoction of tea is precipitated at the boiling heat with acetate of lead; the filtered liquid left to stand for 24 hours, and again filtered to separate a small sediment; the clear solution mixed

with a quantity of ammonia sufficient to neutralise the acid reaction; the yellow precipitate stirred up with absolute alcohol, and decomposed by sulphuretted hydrogen; and the filtrate left to evaporate in vacuo over oil of vitriol. The residue is dissolved in water, and the solution is left to evaporate in vacuo, then dried at 100°, this treatment being repeated three times and the residue finally left for three weeks in vacuo.

*Properties.* When pulverised, it is of a pale yellow colour, like quercitannic acid. Melts at 100° into a mass which draws out into threads. It cakes together when exposed to the air, even for a few minutes, and deliquesces very quickly. Colours ferric hydrochlorate brown, without precipitation.

| | | | Rochleder. |
|---|---|---|---|
| 14 C | 84 | 44·21 | 44·2 |
| 10 H | 10 | 5·26 | 5·8 |
| 12 O | 96 | 50·53 | 50·0 |
| $C^{14}H^{10}O^{12}$ | 190 | 100·00 | 100·0 |

Rochleder assumes for the hypothetical anhydrous acid the formula $C^{7}H^{4}O^{5}$.

*Decompositions.* By dry distillation it yields a light charcoal, and a distillate which smells of acetic acid and blackens iron salts. The aqueous and alcoholic solutions decompose when evaporated in contact with the air.

*Combinations.* The acid dissolves in water in all proportions.

*Boheate of Baryta.* — The lead-salt suspended in alcohol is decomposed by sulphuretted hydrogen; the filtrate mixed with water, is treated with baryta-water, in sufficient quantity to produce a slight alkaline reaction; and the yellow precipitate is washed out of contact with the air, with water containing alcohol.

| | | | Rochleder. |
|---|---|---|---|
| 2 BaO | 153·2 | 44·62 | 44·30 |
| 14 C | 84·0 | 24·48 | 24·32 |
| 10 H | 10·0 | 2·91 | 3·08 |
| 12 O | 96·0 | 27·99 | 28·30 |
| $C^{14}H^{8}Ba^{2}O^{12}$ + 2Aq | 343·2 | 100·00 | 100·00 |

*Boheate of Lead.* — *a. Bibasic.* — The yellow precipitate of crude boheate of lead obtained in the preparation of the acid, on neutralising the liquid with ammonia, is suspended in alcohol and decomposed by sulphuretted hydrogen; the filtrate is freed from sulphuretted hydrogen by leaving it in vacuo over strong potash-solution, then precipitated with alcoholic acetate of lead; and the precipitate is washed with alcohol and dried at 100°. White with a tinge of grey.

| | | | Rochleder. |
|---|---|---|---|
| 2 PbO | 223·6 | 54·06 | 52·00 |
| 14 C | 84·0 | 20·30 | 21·33 |
| 10 H | 10·0 | 2·42 | 2·68 |
| 12 O | 96·0 | 23·22 | 23·99 |
| $C^{14}H^{8}Pb^{2}O^{12}$ + 2Aq | 413·6 | 100·00 | 100·00 |

*b. Basic.* — A decoction of tea is precipitated by neutral acetate of lead; the yellow precipitate suspended in absolute alcohol and decomposed by sulphuretted hydrogen; the filtrate evaporated in vacuo over oil of vitriol; the residue dissolved in water; and the solution precipitated by an ammoniacal solution of acetate of lead.

Egg-yellow precipitate.

| | | | Rochleder. |
|---|---|---|---|
| 4 PbO | 447·2 | 72·22 | 71·43 |
| 14 C | 84·0 | 13·56 | 14·04 |
| 8 H | 8·0 | 1·29 | 1·39 |
| 10 O | 80·0 | 12·93 | 13·14 |
| $C^{14}H^{8}Pb^{2}O^{12},2PbO$ | 619·2 | 100·00 | 100·00 |

In one preparation, Rochleder obtained a salt having the composition $C^{14}H^{16}O^{8},2PbO$; but he did not succeed in preparing it a second time.

Boheic acid dissolves in *alcohol* in all proportions.

# ADDITIONS TO VOL. VII.

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*Formation of Organic Compounds from Inorganic Materials.* — When a mixture of bisulphide of carbon and sulphuretted or phosphuretted hydrogen is passed over copper at a dull red heat, hydrogen gas and marsh gas are obtained, together with a perceptible quantity of olefiant gas and a trace of naphthalin. A somewhat larger quantity of olefiant gas may be produced by the action of a mixture of bisulphide of carbon, sulphuretted hydrogen and carbonic oxide upon iron.

Formic acid is produced by the action of carbonic oxide on potash (x, 490); formiate of baryta yields by dry distillation, marsh-gas, olefiant gas and propylene-gas $C^6H^6$; and the last two hydrocarbons may be converted into the corresponding alcohols by uniting them with sulphuric acid or with hydracids (x, 511, 550). Moreover, a mixture of carbonic oxide and marsh-gas passed through a tube heated to dull redness yields a small quantity of propylene-gas. Further, acetic acid may be formed from alcohol, which may itself be produced from olefiant gas; and acetate of soda subjected to dry distillation, yields olefiant gas (in small quantity) propylene, butylene, and a small quantity of amylene. — Hence and from the known relations between hydrocarbons and alcohols, and between the alcohols and other organic compounds, it appears that a large number of organic compounds may now be formed from inorganic materials. (Berthelot, *Compt. rend.* 43, 236; *Ann. Pharm.* 100, 122.)

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*Synthesis of Methylic Alcohol.* — Marsh-gas mixed with chlorine and exposed to sunshine, yields chloride of methyl together with other substitution products, and chloride of methyl may be converted into methylic alcohol by processes to be presently described.

1. To prepare chloride of methyl in this manner, 40 litres of chlorine are mixed, in bottles each holding a litre, with 40 litres of marsh-gas pre-

viously purified by passing through oil of vitriol and collected over water. The bottles carefully closed are placed so as to receive the sun's rays reflected from a wall; and, as soon as the colour of the chlorine is no longer visible, they are opened under a mercury, and pieces of hydrate of potash are introduced together with a few drops of water. The volume of the gas is thereby reduced one-half, and the residual gas which contains the chloride of methyl, together with unaltered marsh-gas and sometimes hydrogen, is agitated with glacial acetic acid (250 grm. to 8 litres of the residual gas), which absorbs the chloride of methyl together with other gases. On subsequently boiling the acetic acid, the greater part of the absorbed gas escapes; and the remaining portion, which may be expelled by saturating the acid with strong soda-ley, exhibits, after being freed from vapour of acetic acid by contact with sticks of potash, the composition and properties of pure chloride of methyl.

2. Chloride of methyl may be converted into methylic alcohol: *a.* By dissolving it in acetic acid and heating the solution to 200° with acetate of soda; acetate of methyl is then formed, from which the alcohol is easily obtained. This method however is not adapted for large quantities. — *b.* By heating it with aqueous potash to 100° for a week:

$$C^2H^3Cl + KO + HO = C^2H^4O^2 + KCl.$$

2 litres of the gas thus treated, yielded 2 grammes of wood-spirit. — *c.* By treating the chloride with a mixture of oil of vitriol and mercuric-sulphate or sulphate of silver at 100°; methylosulphate of silver is then formed, from which the barium-salt is easily obtained, and from this, methylic alcohol, or benzoate or oxalate of methyl may be obtained. (Berthelot, *Compt. rend.* 45, 916; *Ann. Pharm.* 105, 241.)

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*Preparation of Formic acid.* — Oxalic acid is resolved by heat into carbonic acid, carbonic oxide and water;

$$C^4H^2O^8 = 2CO^2 + 2CO + 2HO.$$

and, as first observed by Gay-Lussac (vii, 269), a small portion of the carbonic oxide unites with water, producing formic acid $C^2H^2O^4$. Now Berthelot has shown that when this decomposition takes place in presence of glycerin, the whole of the carbonic oxide is converted into formic acid. When equal weights of commercial oxalic acid and syrupy glycerin (a kilogramme of each) and from 100 to 200 grammes of water are gently heated (scarcely above 100°) in a capacious retort, a brisk evolution of carbonic acid soon begins, and after 12 or 15 hours, the whole of the oxalic acid is decomposed, half its carbon being given off in the form of carbonic acid, while the remainder produces formic acid in the manner just mentioned. A small quantity of this formic acid distils over with the water, but the larger portion remains in the retort together with the glycerin, and may be separated by distilling the residue with half a litre of water, and renewing the water as it distils, till 6 or 7 litres of

liquid have passed over. The glycerin which then remains may be used for the conversion of fresh quantities of oxalic acid into formic acid.—It is important that the oxalic acid be slowly decomposed; if too much heat is applied, the evolution of carbonic acid becomes stronger, and after this has ceased, the temperature rises to between 190° and 200°, and carbonic oxide is given off, arising from the decomposition of the formic acid dissolved in the glycerin.—Formic acid is almost completely resolved into water and carbonic oxide gas, by heating it to a temperature between 200 and 250° in sealed tubes. (Berthelot, *N. Ann. Chim. Phys.* 46, 477; *Ann. Pharm.* 98, 139.)

Formiate of baryta is decomposed by protochloride of sulphur, yielding formic acid and carbonic oxide gas, together with chloride of barium and sulphate of baryta, and separation of free sulphur;

$$4C^2HBaO^4 + 3ClS = 2C^2H^2O^4 + 4CO + 3BaCl + BaO,SO^3 + 2S.$$

Concentrated formic acid may be prepared by mixing 4 At. of a dry formiate with 4 At. water, gradually adding 3 At. chloride of sulphur, distilling between 110° and 120°, and rectifying the distillate over a small quantity of formiate of lead. (Heintz, *Pogg.* 98, 458.)

*Thioformic acid.*—$C^2H^2S^2O^2$.—Produced in small quantity in the decomposition of formiate of lead by sulphuretted hydrogen, at temperatures above 100°, especially between 200° and 300°. Crystallises in needles from the distilled formic acid, and may be recrystallised from alcohol. Has a slightly alliaceous odour. Melts at about 120°, and sublimes in small transparent crystals even at lower temperatures. The alcoholic solution does not change the colour of litmus.

| | | | | Limpricht. |
|---|---|---|---|---|
| 2 C | 12 | 19·3 | | |
| 2 H | 2 | 3·2 | | |
| 2 S | 32 | 25·9 | | |
| 2 O | 16 | 51·6 | 51·2 | 52·5 |
| $C^2H^2S^2O^2$ | 62 | 100·0 | | |

The acid dissolves in oil of vitriol at a gentle heat, giving off sulphurous acid and depositing sulphur. Strong hydrochloric acid does not act upon it, even at the boiling heat. Nitric acid with the aid of heat destroys it readily, forming sulphuric acid. Strong acetic acid dissolves it in small quantity and deposits it unchanged on cooling. Heated with sulphuric acid and chromate of potash, it reduces the chromic acid to chromic oxide; peroxide of lead is partially reduced in like manner. Fused with hydrate of potash, it forms a reddish yellow mass which, when treated with dilute sulphuric acid, gives off sulphuretted hydrogen and an odour of garlic. Potash-ley dissolves but little of it, even at the boiling heat; and the solution treated with acids, gives off traces of sulphuretted hydrogen. The acid does not dissolve in sulphide of ammonium either hot or cold.

Thioformic acid is insoluble in water, and nearly insoluble in cold alcohol and ether; but dissolves pretty readily in those liquids at the boiling heat: part of it volatilises with the alcohol vapour.

The alcoholic solution is not altered by sesquichloride of iron; it forms with neutral acetate of *lead*, a yellowish precipitate which turns black when heated with the liquid; with nitrate of *silver*, an amorphous precipitate, which is white at first, but soon turns black, and dissolves partially in hot alcohol, with separation of metallic silver or sulphide of silver.

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*Action of Heat on Chloride of Methyl.* — When chloride of methyl is passed through a red-hot porcelain tube, and the gaseous products of decomposition, after being washed with a large quantity of water to absorb hydrochloric acid, and then dried over chloride of calcium, are made to pass into a long-necked vessel containing bromine, thence into a cooled receiver, and finally into solution of potash to absorb the excess of bromine, the following products are obtained: 1. A considerable quantity of carbon is deposited in the porcelain tube together with a small quantity of a liquid having an empyreumatic odour; crystals of naphthalin are deposited in the tube which conveys the gases into the wash-bottle. — 2. The bromine, which is not altered in appearance, yields, when treated with very dilute potash, a liquid heavier than water, insoluble in water, but soluble in alcohol and ether; and this liquid, by repeated distillation yields a liquid having an ethereal odour, and boiling a little above 150°, and a solid product which melts at about 40°, boils at 220°, has an agreeable odour, is unctuous to the touch and very permanent. The solid body yielded by analysis 21·64 p. c. carbon 1·61 hydrogen, and 76·68 bromine, numbers which do not lead to any simple formula. — The liquid boiling at 150°, gave, as the mean of two analyses, 13·44 p. c. C, 2·23 H and 85·1 Br., numbers agreeing nearly with the composition of bromide of ethylene, $C^4H^4$ Br. — It appears probable therefore that the chloride of methyl is resolved at a red heat into methylene $C^2H^2$, and hydrochloric acid, but that the methylene, at the moment of separation, doubles its molecule and becomes converted into ethylene. A portion of it also undergoes decomposition, as shown by the presence of naphthalin and other products. — 3. The gas collected after the excess of bromine has been absorbed by the potash, exhibits nearly the composition of methylene, but really consists of a mixture of marsh-gas and oxide of carbon, the latter being formed by the action of the red-hot carbon in the tube on carbonic acid gas given off by the mixture which yields the chloride of methyl, and possibly on a small quantity of aqueous vapour. (A. Perrot, *N. Ann. Chim. Phys.* 49, 94.)

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## Methylophosphorous Acid.

$C^2H^5PO^6 = P(C^2H^3)H^2O^6$.

HUGO SCHIFF. *Ann. Ch. Pharm.* 103, 164.

*Formation.* By the action of terchloride of phosphorus on methylic alcohol:

$$3C^2H^4O^2 + PCl^3 = C^2H^5PO^6 + 2C^2H^3Cl + HCl.$$

*Preparation.* When terchloride of phosphorus is added by drops to wood-spirit, a strong action takes place, the liquid becoming strongly heated and gradually assuming a red colour (arising probably from the presence of hydrocarbons, and scarcely perceptible when pure methylic alcohol is used.) The addition of the terchloride of phosphorus is continued as long as any action takes place, and the liquid is then left in a warm place for several hours, to expel hydrochloric acid and excess of methylic alcohol. The compound is thus obtained in the form of a nearly colourless, very acid syrup, which draws out into threads, and cannot be made to crystallise. On attempting to concentrate it further by heat, it is resolved into methylic alcohol and phosphorous acid.

The *Methylophosphites*, $P(C^2H^3)HMO^6$, are obtained by treating the corresponding carbonates with the aqueous acid. By evaporation at ordinary temperatures or at a very gentle heat, they are obtained as amorphous masses which exhibit crystalline structure when scratched with a sharp-edged tool. When strongly heated, they give off phosphuretted hydrogen and combustible hydrocarbons, leaving a residue of phosphate mixed with a little amorphous phosphorus. They are hygroscopic, and dissolve readily in water, sparingly in alcohol, and not at all in ether. The aqueous solutions decompose slowly at ordinary temperatures into methylic alcohol and phosphites. This decomposition takes place most quickly when the solutions are acid, and may be prevented by keeping an excess of the carbonate in the liquid during evaporation.

*Baryta-salt.* — Anhydrous; less soluble in water and alcohol than the lime-salt.

| | | | Schiff. |
|---|---|---|---|
| P | 31·4 | 19·1 | 19·12 |
| $C^2H^3$,H | 16·0 | 9·8 | |
| Ba | 68·6 | 41·8 | 41·17 |
| 6 O | 48·0 | 29·3 | |
| $P(C^2H^3)HBaO^6$ | 164·0 | 100·0 | |

An attempt to prepare a bibarytic salt, by treating a solution of this salt with strong baryta-water did not succeed. The liquid, after 24 hours, deposited a considerable quantity of baryta, and the filtrate when evaporated left the original salt.

*Lime-salt.* — Contains 2 At. water, which it gives off at 100°.

| | | | Schiff. |
|---|---|---|---|
| P | 31·4 | 23·5 | 23·35 |
| $C^2H^3,H$ | 16·0 | 12·0 | |
| Ca | 20·0 | 15·0 | 15·00 |
| 6 O | 48·0 | 36·0 | |
| 2 HO | 18·0 | 13·5 | 13·80 |
| $P(C^2H^3)HCaO^6 + 2Aq$ | 133·4 | 100·0 | |

*Lead-salt.* $P(C^2H^3)HPbO^6$. — Very easily decomposed. When the solution is evaporated at a gentle heat, a mass remains which melts between 55° and 60°, and gives off water and combustible hydrocarbons between 60° and 70°. Above 80°, the decomposition goes on very rapidly; but no evolution of phosphuretted hydrogen takes place till the salt is heated considerably above 110°. The salt gave by analysis 0·129 grm. of phosphorus to 0·432 grm. of lead; the calculated quantity is 0·1304 grm. of phosphorus.

The solution of the lime-salt does not precipitate the chlorides of copper and iron; with *mercuric* chloride it forms a white precipitate; and with nitrate of silver, a precipitate which is white at first but quickly yields reduced silver.

## Methylophosphoric Acids.

Hugo Schiff. *Ann. Pharm.* 102, 334.

*Formation and Preparation.* By the action of chlorophosphoric acid on methylic alcohol:

$$PO^2Cl^3 + 3C^2H^4O^2 = \underbrace{P(C^2H^3)H^2O^8}_{\text{monomethylo-phosphoric acid.}} + 2C^2H^3Cl + HCl.$$

and:

$$PO^2Cl^3 + 3C^2H^4O^2 = \underbrace{P(C^2H^3)^2HO^8}_{\text{bimethylophos-phoric acid.}} + C^2H^3Cl + 2HCl.$$

On mixing the two liquids, great heat is evolved, vapours of hydrochloric acid and chloride of methyl are given off, and a dark red liquid remains consisting of mono- and bi-methylophosphoric acids, the former being in the greater quantity. But, if the chlorophosphoric acid be placed in a flask attached to the lower end of a condensing apparatus, and standing in cold water, and the wood-spirit be added by drops from the upper end, each addition being made only after the reaction produced by the former has subsided, the product consists almost entirely of bimethylophosphoric acid, which, after the red liquid has been freed from hydrochloric acid and wood-spirit by heating it for several hours in the water-bath, remains in the form of a colourless syrup, but by continued heating over the water-bath is gradually resolved into wood-spirit and phosphoric acid.

*Bimethylophosphoric acid* is very sour, attacks zinc with evolution of hydrogen, and decomposes carbonates with facility. The aqueous solution is readily decomposed by boiling, apparently with formation of monomethylophosphoric acid. It is soluble in alcohol and ether.

The *Bimethylophosphates* $P(C^2H^3)^2MO^8$, are obtained by neutralising the aqueous acid with the corresponding carbonates. Some of the less soluble may also be obtained by precipitation. They are easily separated from the monomethylophosphates, which are much less soluble and separate out on evaporation. The bimethylophosphates are mostly colourless, dissolve pretty readily in water, less in alcohol, not at all in ether, and are precipitated by alcohol and ether from their concentrated solutions. — Almost all of them contain several atoms of water of crystallisation. — Their aqueous solutions are decomposed by evaporation unless the heat is kept very low. By distillation they yield the same products as the free acid, with a residue of phosphate.

*Baryta-salt.* $P(C^2H^3)^2BaO^8$. — Micaceous laminæ nearly insoluble in alcohol, and containing 35·0 p. c. Ba and 15·6 p. c. P (by calculation 35·4 Ba and 16·2 P).

*Strontia-salt.* — Somewhat more soluble in alcohol than the baryta-salt, and crystallises from the alcoholic solution by gradual evaporation in silky crystalline laminæ arranged in radiated groups. Gives off 2 At. water at 160°.

| | *Dried over oil of vitriol.* | | Limpricht. |
|---|---|---|---|
| P | 31·4 | 16·7 | 16·7 |
| $2\ C^2H^3$ | 30·0 | 16·0 | |
| Sr | 43·8 | 23·4 | 22·7 |
| 8 O | 64·0 | 34·2 | |
| 2 HO | 18·0 | 9·7 | 9·65 |
| $P(C^2H^3)^2SrO^8 + 2Aq$ | 187·2 | 100·0 | |

*Lime-salt.* $P(C^2H^3)^2CaO^8$. — Separates in warty masses, very soluble in water. Contains 13·54 p. c. Ca and 20·8 P (by calculation, 13·7 Ca and 28·6 P).

*Magnesia-salt.* — White powder, soluble in water.

*Zinc-salt.* — White and pretty readily soluble.

The *Iron* and *Copper salts* appear also to be easily soluble, inasmuch as the solution of the lime-salt is not precipitated by solutions of iron or copper.

*Lead-salt.* $P(C^2H^3)^2PbO^8$. — Precipitated from the concentrated aqueous solution by ether in flakes containing 45·07 p. c. of lead (calculation, 45·34 p. c.).

The soluble bimethylophosphates form white precipitates with salts of cobalt, mercury and silver.

*Monomethylophosphoric acid.* $P(C^2H^3)H^2O^8$.— Obtained together with bimethylophosphoric acid (p. 482); also by the action of pentachloride of phosphorus on wood-spirit, chlorophosphoric acid being first produced, as shown by the equation.

$$PCl^5 + C^2H^4O^2 = PO^3Cl^3 + C^2H^3Cl + HCl,$$

and then acting on the rest of the methylic alcohol as above. The action is violent and attended with great evolution of heat.

The *Monomethylophosphates*, $P(C^2H^3)H^2O^8$, are much less soluble in water than the bimethylophosphates. The *baryta-salt* is less soluble in water at 100° than in luke-warm water. It therefore separates as soon as the solution is placed over the water-bath, in laminæ having a strong lustre. It gives off the greater part of its water of crystallisation, even on exposure to the air, a further portion over sulphuric acid, losing its lustre at the same time, and the whole (4 At.) at 150°. When strongly heated, it gives off combustible gases.

| | *Crystallised.* | | | Limpricht. |
|---|---|---|---|---|
| P | 31·4 | .... | 11·1 | |
| $C^2H^3$ | 15·0 | .... | 5·2 | |
| 2 Ba | 137·2 | .... | 48·4 | ..... 48·8 |
| 8 O | 64·0 | .... | 22·6 | |
| 4 HO | 36·0 | .... | 12·7 | ..... 14·8 |
| $P(C^2H^3)Ba^2O^8 + 4Aq$ | 283·6 | .... | 100·0 | |

Sulphochloride of phosphorus forms with methylic alcohol an acid ether, whose baryta-salt is soluble in water and probably consists of $P(C^2H^3)H^2S^2O^6$.

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## Bisulphometholic Acid.

$C^2H^4S^4O^{12} = C^2H^4,4SO^3$.

BUCKTON & HOFMANN. *Phil. Trans.* 1856, 1; *Chem. Soc. Qu. J.* 9, 241; *Ann. Pharm.* 100, 129.
STRECKER. *Ann. Pharm.* 100, 199.

*Disulphometholic acid, Methylotetrasulphuric acid* (x, 497), *Methionic acid.*

*Formation.* 1. By the action of fuming sulphuric acid on acetonitrile (cyanide of methyl) or acetamide, sulphacetic acid being formed at the same time:

$$\underbrace{C^4NH^3}_{\text{acetonitrile.}} + 6SO^4H = \underbrace{C^2H^4S^4O^{12}}_{\text{bisulphometholic acid.}} + \underbrace{NH^4,H,2SO^4}_{\text{sulphate of ammonia.}} + 2CO^2.$$

and:

$$C^4NH^3 + 4SO^4H + 2HO = \underbrace{C^4H^4O^4,2SO^3}_{\text{sulphacetic acid.}} + NH^4,H,2SO^4.$$

Since acetamide, $C^4NH^5O^2$, differs from acetonitrile only by 2HO, its decomposition by sulphuric acid will be represented by nearly the same equations. — If the two bodies are very carefully mixed, and the mixture is cooled from time to time, scarcely any carbonic acid is evolved, and the product then consists chiefly of sulphacetic acid; but if the heat be greatly increased, carbonic

acid escapes and the product is chiefly bisulphometholic acid. The reaction appears indeed to consist of two stages. In the former, the nascent acetic acid simply unites with $2SO^3$; in the latter, the acetic acid is resolved into carbonic acid and marsh-gas, the latter combining with $4SO^3$. (Bisulphometholic acid cannot however be formed by the direct combination of marsh-gas with sulphuric acid. (Buckton and Hofmann.)

3. By the action of anhydrous sulphuric acid on ether. This was the process by which Liebig first obtained the acid (methionic acid, viii, 435). It is merely a secondary product of the reaction, the principal product being neutral sulphate of ethyl (viii, 413). The acid thus obtained has since been examined by Wetherill and by Redtenbacher, and more completely by Strecker. Buckton & Hofmann have shown that it is identical with bisulphometholic acid.

*Preparation.* 1. Acetonitrile and fuming sulphuric acid may be mixed completely and almost without colour in a vessel externally cooled (without this precaution, the heat evolved causes a large portion of the acetonitrile to volatilise); but if the mixture be then strongly heated, it swells up considerably and gives off a large quantity of carbonic acid gas. The residue when cold forms a thick brown transparent mass, which dissolves readily in water or alcohol. Its aqueous solution boiled with carbonate of baryta and filtered hot, yields bisulphometholate of baryta in beautiful crystals; and on decomposing this salt with a slight excess of sulphuric acid, saturating the filtrate with oxide of lead, precipitating the lead with sulphuretted hydrogen, concentrating the liquid to a syrup, and leaving it to evaporate in vacuo, the acid is obtained in the crystalline state. — 2. A mixture of 2 vol. acetamide and 3 vol. fuming sulphuric acid (equal volumes yield scarcely anything but acetic acid and sulphate of ammonia) is heated till sulphurous acid begins to appear among the products of distillation; the residue is dissolved in water; the free sulphuric acid neutralised with finely pounded marble; the liquid boiled with carbonate of baryta to decompose the sulphate of ammonia; and the filtrate evaporated to the crystallising point. It then yields crystals of bisulphometholate of ammonia, while sulphacetate of ammonia remains in the mother-liquor. A moderately concentrated solution of the ammonia-salt mixed with a saturated solution of acetate or chloride of barium, yields crystals of the barium-salt of bisulphometholic acid, from which the free acid may be obtained as above. (Buckton & Hofmann.)

3. A flask filled with anhydrous sulphuric acid is inverted in a glass cylinder containing a little ether, and left there till all the acid has disappeared; after which the product is shaken up with water, and the watery liquid separated from the ethereal solution of neutral sulphate of ethyl is treated with carbonate of baryta, &c., as above. The ethereal solution also contains methionic acid. Another method is to pass the vapour of anhydrous sulphuric acid into cold anhydrous ether; but the former yields a better product. (Strecker.)

*Properties.* The acid obtained by evaporating the aqueous solution in vacuo, forms long needle-shaped crystals, which are highly deliquescent and have a very sour taste. (Buckton & Hofmann, Strecker.) — The aqueous solution may be boiled with nitric acid, or chlorine gas may be passed through it, without any separation of sulphuric acid ensuing. (Buckton & Hofmann.)

The *Bisulphetholates* or *Methionates* are obtained by digesting the aqueous acid with oxides or carbonates; they are all soluble in water, but insoluble in alcohol, at least in absolute alcohol.

*Ammonia-salt.* (*Preparation*, p. 485). — Dissolves with moderate facility in cold water, very easily in hot water. The boiling solution deposits colourless prisms with dihedral summits, and sometimes an inch long. (B. & H.) Sustains a heat of 140° (Strecker), 190° (B. & H.), without alteration.

| | *At* 190°. | | Buckton & Hofmann (*mean*). |
|---|---|---|---|
| 2 C | 12 | 5·71 | 5·32 |
| 10 H | 10 | 4·76 | 5·22 |
| 2 N | 28 | 13·33 | 12·98 |
| 4 S | 64 | 30·47 | 30·55 |
| 12 O | 96 | 45·73 | 45·93 |
| $C^2H^2(NH^4)^2,4SO^3$ | 210 | 100·00 | 100·00 |

*Potash-salt.* — Easily obtained by gradually mixing a boiling solution of carbonate of potash with a solution of the baryta-salt, avoiding an excess of the latter. The alkaline filtrate deposits the salt in shining needles or in granules, accordingly as it separates from solution quickly or slowly. (B. & H.) Anhydrous; crystallises in long needles. (Strecker.) 1 pt. of the salt dissolves in 14 pts. of water at 220°. (B. & H.)

*Baryta-salt.* (*Preparation*, p. 485). — Crystallises in rectangular plates having a mother-of-pearl lustre, and giving off the whole of their water, amounting to 10·54 p. c. (4 At.) at 150°. (B. & H.) Very thin rhombic tables which exhibit very beautifully the colours of thin plates, and have a mother-of-pearl lustre when dry. The salt does not alter in appearance or in weight at 130°, but gives off its 4 At. water at 140°. At a higher temperature, it decomposes without fusion and gives off sulphur. Ignited in contact with the air, it leaves sulphate of baryta, which however is difficult to free from a mixture of sulphide and sulphite. Fused with hydrate of potash, it leaves a mixture of sulphite and sulphate in nearly equal numbers of atoms. (Strecker.) [According to Liebig (viii, 435) sulphurous acid is not formed in this reaction.

| | *Anhydrous.* | | Buckton & Hofmann. | Strecker. |
|---|---|---|---|---|
| 2 C | 12 | 3·85 | 3·71 | 3·4 |
| 2 H | 2 | 0·67 | 0·63 | 0·7 |
| 2 Ba | 137 | 44·05 | 44·05 | 44·0 |
| 4 S | 64 | 20·57 | 20·83 | |
| 12 O | 96 | 30·86 | 30·78 | |
| $C^2H^2Ba^2,S^4O^{12}$ | 311 | 100·00 | 100·00 | |

| | | | Strecker. | Liebig. | Redtenbacher. | Wetherill. |
|---|---|---|---|---|---|---|
| 2 C | 12 | 3·46 | | 3·5 | 3·4 | 2·8 |
| 6 H | 6 | 1·73 | | 1·8 | 1·8 | 1·9 |
| 2 Ba | 137 | 39·48 | 39·5 | 39·2 | | 39·6 |
| 4 S | 64 | 18·44 | | | 18·6 | |
| 16 O | 128 | 36·89 | | | | |
| $C^2H^2Ba^2S^4O^{12} + 4Aq$ | 347 | 100·00 | | | | |

*Lime-salt.* — Crystallises in delicate silky needles, very soluble in water. (Strecker.)

*Zinc-salt.* — Metallic zinc dissolves in the aqueous acid, with evolution of hydrogen; and the solution when evaporated yields a syrup which crystallises with great difficulty. The solution is not precipitated by alcohol. (Buckton & Hofmann.)

*Lead-salt.* — *a. Neutral.* $C^2H^2Pb^2S^4O^{12}+4Aq$. — Obtained by decomposing the baryta-salt with sulphuric acid and boiling the filtrate with carbonate of lead. The solution concentrated by evaporation and slowly cooled, yields the salt in large, transparent, colourless, rhombic prisms, probably isomorphous with the barium-salt. (Strecker.) Small square nacreous laminæ resembling those of the barium-salt. (B. & H.) The crystals do not alter in the air at ordinary temperatures, but at 100° they give off 8·4 p.c. (4 At.) water; no further loss of weight takes place at 160°. The anhydrous salt gives by analysis 58·5 p. c. PbO, agreeing exactly with the formula $C^2H^2Pb^2S^4O^{12}$. The salt dissolves very easily in water and is precipitated from the solution by alcohol. (Strecker.)

*b. Basic.* $PbO,C^2H^2Pb^2S^4O^{12}+Aq$ ? — Obtained by boiling the neutral salt with hydrated oxide of lead. It is much less soluble in water than the neutral salt and separates from the hot solution in colourless crystals on cooling. Has an alkaline reaction and absorbs carbonic acid from the air. After drying over oil of vitriol, it gives off 2·1 p. c. water (1 At.; calculation 1·9) at 120°. The anhydrous salt gave by analysis 69·2 p. c. PbO (calculation, 68 p. c.). The salt was probably contaminated with carbonate of lead. (Strecker.)

*Copper-salt.* $C^2H^2Cu^2S^4O^{12}+10Aq$. — Obtained by decomposing the baryta-salt with sulphate of copper. Crystallises in blue rhombic prisms which effloresce and turn white when exposed to the air. (Strecker.) Needles united in radiating groups, or small prisms of a green colour. (B. & H.) Soluble in dilute alcohol, insoluble in absolute alcohol. (Strecker, B. & H.) Gives off 26·2 p. c. water (10 At.; by calculation 27·5 p. c.) and suffers no further loss at 160°. The anhydrous salt gave by analysis 33·6 p. c. CuO (calculation 33·4 p. c.) (Strecker.)

*Silver-salt.* — Obtained by neutralising the aqueous acid with oxide or carbonate of silver. Crystallises in groups of slender needles or broad plates of considerable size, but usually much modified and with rounded edges. (Buckton & Hofmann.) Thin colourless laminæ, which in the moist state are somewhat blackened by exposure to light. (Strecker.) The salt sustains a heat of 140° without decomposition, but blackens and froths at a higher temperature, giving off sulphurous acid and sulphur, and leaving metallic silver. Insoluble in absolute alcohol, but may be crystallised from dilute alcohol. (B. & H.) Alcohol precipitates it from the concentrated aqueous solution. (Strecker.)

| | *At* 120°. | | | Buckton & Hofmann. | Strecker. |
|---|---|---|---|---|---|
| 2 C | 12 | | 3·07 | 2·97 | |
| 2 H | 2 | | 0·51 | 0·58 | |
| 2 Ag | 216 | | 55·37 | 55·41 | 55·35 |
| 4 S | 64 | | 16·41 | | |
| 12 O | 96 | | 24·64 | | |
| $C^2H^2Ag^2S^4O^{12}$ | 390 | | 100·00 | | |

Buckton & Hofmann did not succeed in preparing the ethers of bisulphometholic acid.

## Methylobithionic Acid. $C^2H^4S^2O^4$.

J. T. Hobson. *Chem. Soc. Qu. J.* 10, 243.

*Methylodithionic acid.*

*Formation and Preparation.*—By the action of sulphurous acid on zinc-methyl. Dry sulphurous acid passed into an ethereal solution of zinc-methyl, kept cool to moderate the action, is rapidly and completely absorbed, and in a little while, a white crystalline substance is formed, which is the zinc-salt of methylobithionic acid, $C^2H^3ZnS^2O^4$. This salt may be freed from ether and the last traces of sulphurous acid by evaporation in vacuo. It may then be converted into a baryta-salt by treating it with excess of caustic baryta, and from this the acid may be prepared by precipitating the baryta with dilute sulphuric acid.

*Properties.* Liquid, having a feebly acid taste and reddening blue litmus. It decomposes in a short time, with deposition of sulphur, even in a very dilute solution.

The *Methylobithionates* cannot be conveniently prepared by digesting the free acid with oxides or carbonates, on account of the facility with which the acid decomposes; but they may be obtained by decomposing the zinc-salt with the corresponding bases, or the baryta-salt with the sulphates. Their general formula is $C^2H^3MS^2O^4$. [Hobson regards the hypothetical anhydrous acid as formed from 2 At. sulphurous acid $S^2O^4$, by the substitution of 1 At. methyl for 1 At. oxygen, making the formula of the methylobithionates $MO,S^2.\left\{\begin{matrix}C^2H^3\\O^3\end{matrix}\right\}$. They are all very soluble in water but insoluble in alcohol and ether.

*Methylobithionate of Baryta.*—Prepared by treating the solution of the zinc-salt with excess of caustic baryta, filtering to separate oxide of zinc, precipitating the excess of baryta by a stream of carbonic acid, and evaporating the filtrate at the heat of the water-bath.

Colourless, inodorous, crystalline salt, which is precipitated from its strong aqueous solution by alcohol in the form of a white granular powder. A concentrated aqueous solution left to evaporate in vacuo, deposits the salt in cubes arranged in octohedral masses. It sustains a heat of 170° without decomposition.

| | *At* 100°. | | Hobson. |
|---|---|---|---|
| 2 C | 12·0 | 8·13 | 7·86 |
| 3 H | 3·0 | 2·03 | 2·17 |
| Ba | 68·6 | 46·48 | 46·30 |
| 2 S | 32·0 | 21·68 | 21·66 |
| 4 O | 32·0 | 21·68 | 22·01 |
| $C^2H^3BaS^2O^4$ | 147·6 | 100·00 | 100·00 |

*Methylobithionate of Lime.*—Obtained by treating the zinc-salt with excess of lime-water, and precipitating the lime from the filtrate by carbonic acid. A concentrated solution left to evaporate in vacuo deposits the salt as a solid mass which does not crystallise. It is inodorous and has a disagreeable somewhat bitter taste.

| | *At* 100°. | | Hobson. |
|---|---|---|---|
| 2 C | 12 | 12·12 | 12·00 |
| 3 H | 3 | 3·03 | 3·29 |
| Ca | 20 | 20·20 | 19·64 |
| 2 S | 32 | 32·32 | |
| 4 O | 32 | 32·33 | |
| $C^2H^3CaS^2O^4$ | 99 | 100·00 | |

*Methylobithionate of Magnesia.* — Obtained by decomposing the baryta-salt with sulphate of magnesia or the zinc-salt with caustic magnesia. — Colourless, inodorous salt, which separates from its aqueous solution by evaporation in a mass of minute crystals which retain 1 At. water at 100°.

| | *At* 100°. | | Hobson. |
|---|---|---|---|
| 2 C | 12 | | 11·64 |
| 4 H | 4 | | 4·00 |
| Mg | 12 | | 12·00 |
| 2 S | 32 | | 31·47 |
| 5 O | 40 | | 40·89 |
| $C^2H^3MgS^2O^4$ + Aq | 100 | | 100·00 |

*Methylobithionate of Zinc.* — (*Preparation*, p. 488). — Colourless, inodorous salt, having a bitter, somewhat disagreeable taste. Crystallises from the aqueous solution by evaporation, when the liquid becomes very concentrated, but on account of its great solubility, does not form any large crystals. It is stable at 100°, but decomposes and blackens at a somewhat higher temperature, emitting a most offensive odour.

| | *At* 100°. | | Hobson. |
|---|---|---|---|
| 2 C | 12·0 | 10·76 | 10·72 |
| 3 H | 3·0 | 2·69 | 2·61 |
| Zn | 32·5 | 29·15 | 28·97 |
| 2 S | 32·0 | 28·70 | 28·55 |
| 4 O | 32·0 | 28·70 | 29·15 |
| $C^2H^3ZnS^2O^4$ | 111·5 | 100·00 | 100·00 |

*Methylobithionate of Nickel.* — Obtained by decomposing the baryta-salt with sulphate of nickel. Forms a grass-green solution, which when left to evaporate in vacuo, dries up, with partial decomposition, to an amorphous mass of a dirty buff colour.

*Methylobithionate of Copper.* — Prepared like the baryta-salt. Its aqueous solution has a bright green colour, and when evaporated at 100°, becomes brownish yellow, in consequence of decomposition; the dilute solution also decomposes gradually and deposits sulphur even when exposed to the air at common temperatures.

*Methylobithionate of Silver.* — Carbonate of silver dissolves slowly in the free acid, but on evaporating the solution over the water-bath, it decomposes even below the boiling heat. The dilute solution also blackens rapidly when exposed to light.

*Methylobithionate of Ethyl.* — A mixture of methylobithionate of baryta and sulphovinate of potash, yields, when distilled at a high temperature, an oily liquid, together with large quantities of sulphurous acid. The product, after being washed with water, dried over chloride of calcium, and redistilled in vacuo, formed a light straw-coloured liquid slightly heavier than water and having a peculiar fishy odour. It undergoes decomposition at the high temperature required to prepare it.

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## Iodides and Chloriodides of Tetramethylium.

C. WELTZIEN. *Ann. Pharm.* 99, 1.

*Teriodide.* — $(C^2H^3)^4N.I^3$. — When a solution of protiodide of tetramethylium is mixed with an alcoholic solution of iodine containing as much iodine as is required to form the teriodide, the first crop of crystals deposited from the liquid nevertheless consists wholly of pentiodide (x, 498); but afterwards crystals of the teriodide and pentiodide are deposited together and may be separated mechanically and purified by recrystallisation. — The teriodide forms crystals belonging to the right prismatic system, having a deep violet colour and strong lustre; it is more soluble in alcohol than the pentiodide. It gave by analysis 83·7 p. c. iodine, the formula requiring 83·5.

The *Pentiodide*, $(C^2H^3)^4NI^5$, is the only product obtained when an excess of iodine is used. It forms small tabular crystals having a dark greenish-grey colour and perfect metallic lustre. Melts at 120°, and solidifies in a shining crystalline mass. (Compare x, 498.)

*Tetrachloriodide* $(C^2H^3)^4NICl^4$. — On heating the teriodide or pentiodide of tetramethylium with oxide of silver, iodide of silver is immediately formed (together with a small quantity of iodate), and a colourless, strongly alkaline solution is obtained, containing the hydrated oxide and the iodate of tetramethylium:

$$3(C^2H^3)^4NI^3 + 8AgO = (C^2H^3)^4NO,IO^5 + 2(C^2H^3)^4NO + 8AgI:$$

and on gently heating the filtered liquid with hydrochloric acid (best after neutralising it with iodic acid), chlorine is evolved, and the tetrachloride of tetramethylium is deposited as a very loosely coherent, lemon-yellow substance smelling strongly of chloride of iodine:

$$(C^2H^3)^4NIO^6 + 6HCl = (C^2H^3)^4NICl^4 + 2Cl + 6HO.$$

| | | | | Weltzien. |
|---|---|---|---|---|
| 8 C | 48 | 14·0 | | 14·5 |
| 12 H | 12 | 3·6 | | 4·4 |
| N | 14 | 4·0 | | |
| I | 127 | 37·0 | | 36·6 |
| 4 Cl | 142 | 41·4 | | 38·8 |
| $(C^2H^3)^4NICl^4$ | 343 | 100·0 | | 100·0 |

Analogous to Filhol's chloriodide of ammonium $NH^4ICl^4$ (II, 487), and may be regarded as pentiodide of tetramethylium in which 4 At. I are replaced by 4Cl.

*Terchloriodide.* $(C^2H^3)^4NICl^3$. — Obtained: 1. By mixing chloride of tetramethylium with chloride of iodine. — 2. By passing chlorine into a solution of protiodide of tetramethylium; a precipitate of pentiodide is then formed, and afterwards a colourless solution, which, when evaporated, deposits the terchloriodide.

Lemon-yellow substance.

| | | | Weltzien. |
|---|---|---|---|
| 8 C | 48·0 | 15·6 | 15·3 |
| 12 H | 12·0 | 4·0 | 4·3 |
| N | 14·0 | 4·5 | |
| I | 127·0 | 41·5 | 41·6 |
| 3 Cl | 105·5 | 34·4 | 33·4 |
| $(C^2H^3)^4NICl^3$ | 306·5 | 100·0 | |

*Bichloriodide.* $(C^2H^3)^4NICl^2$. — A solution of the terchloriodide in water deposits the bichloriodide, in shining, yellow, inodorous crystals, belonging to the square prismatic system.

| | | | |
|---|---|---|---|
| 8 C | 48 | 17·1 | 17·0 |
| 12 H | 12 | 4·4 | 5·0 |
| N | 14 | 5·1 | |
| I | 127 | 46·9 | 45·1 |
| 2 Cl | 70 | 25·9 | 26·6 |
| $(C^2H^3)^4NICl^2$ | 271 | 100·0 | |

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## Trimethylphosphine. $(C^2H^3)^3.P$.

A. W. Hofmann & A. Cahours. *Phil. Trans.* 1858, 592; *Ann. Pharm.* 104, 29; *Chem. Soc. Qu. J.* 11, 73.

*Formation and Preparation.* By the action of terchloride of phosphorus on zinc-methyl:

$$3C^2H^3Zn + PCl^3 = (C^2H^3)^3P + 3ZnCl.$$

Terchloride of phosphorus is added by drops to an ethereal solution of zinc-methyl contained in a tubulated retort with proper condensing apparatus attached (for the description and figure of the apparatus, see *Triethylphosphine*), a stream of carbonic acid being passed through the apparatus during the whole process. As the action is intensely violent, the terchloride of phosphorus must be dropped in very slowly. When the action is terminated, a heavy oily liquid surmounted by a lighter one, is found in the retort and in the condensing apparatus. The heavy liquid is a compound of trimethylphosphine with chloride of zinc; the lighter is a mixture of ether with excess of terchloride of phosphorus. The latter is decanted, and the compound of trimethylphosphine and chloride of zinc is distilled in a stream of hydrogen, the trimethylphosphine which then passes over being

collected in a receiver surrounded with ice. The stream of hydrogen must be made to flow very slowly; otherwise a considerable quantity of the base will be carried away by it.

*Properties.* Transparent, colourless, mobile liquid, heavier than water, having a strong refracting power, and an indescribably nauseous odour. Boils between 40° and 42°. (Compare vii, 328.) Insoluble in water.

*Binoxide.* — $(C^2H^3)^3PO^2$. — Produced: 1. By the direct oxidation of trimethylphosphine. This substance has a very powerful attraction for oxygen, fuming and sometimes taking fire in contact with the air. — On distilling it, even when recently prepared, the neck of the retort becomes covered in the last stage of the operation, with a beautiful network of crystals of the binoxide; they may readily be obtained in larger quantity by exposing the base to a slow current of dry air. — 2. By the action of heat on the hydrated oxide of tetramethylphosphonium, marsh-gas being given off at the same time:

$$(C^2H^3)^4PO,HO = (C^2H^3)^3PO^2 + C^2H^3,H.$$

*Bisulphide.* — $(C^2H^3)^3PS^2$. — Obtained by gradually adding flowers of sulphur to an ethereal solution of trimethylphosphine, — or by distilling trimethylphosphine with cinnabar. It is not obtained by treating the oxide with sulphuretted hydrogen or sulphide of ammonium. Crystallises from a highly concentrated aqueous solution, in masses of well formed four-sided prisms, which melt at 105°.

*Biselenide.* — $(C^2H^3)^3PSe^2$. — Obtained by the action of selenium on trimethylphosphine. — Crystallises like the ethyl compound (*q. v.*). Melts at 84°. In contact with the air it blackens, with separation of selenium, and gives off the odour of mesitilene (ix, 17).

*Platinum salt.* — The solution of trimethylphosphine in hydrochloric acid, yields with bichloride of platinum, an orange-yellow, indistinctly crystalline precipitate, which is easily decomposed by exposure to 100°.

| *Dried over oil of vitriol.* | | | Hofmann & Cahours. |
|---|---|---|---|
| $(C^2H^3)^3P$ | 76·0 | 26·94 | |
| HCl | 36·5 | 12·93 | |
| 2 Cl | 71·0 | 25·16 | |
| Pt | 98·7 | 34·97 | 34·86 |
| $(C^2H^3)^3P,HCl + PtCl^2$ | 282·2 | 100·00 | |

## Tetramethylphosphonium. $(C^2H^3)^4.P$.

Hofmann & Cahours. *loc. cit.*

Known only in combination.

The *iodide* is obtained by the action of iodide of methyl on an ethereal solution of trimethylphosphine. White crystalline mass, which when recently prepared, exhibits the silvery lustre of sublimed naphthalin, and assumes a slightly reddish colour in contact with the air.

| | | | Hofmann & Cahours. |
|---|---|---|---|
| $(C^2H^3)^4P$ | 91 | 41·75 | |
| I | 127 | 58·25 | 58·14 |
| $(C^2H^3)^4PI$ | 218 | 100·00 | |

Treated with oxide of silver, it yields a very caustic solution of *oxide of tetramethylphosphonium.*

*Gold-salt.* — Obtained by mixing the solution of chloride of tetramethylphosphonium and terchloride of gold. Crystallises from boiling water in brilliant yellow needles.

| | *At* 100°. | | Hofmann & Cahours. |
|---|---|---|---|
| $(C^2H^3)^4P$ | 91 | 21·17 | |
| 4 Cl | 142 | 33·02 | |
| Au | 197 | 45·81 | 45·98 |
| $(C^2H^3)^4P,HCl + AuCl^3$ | 430 | 100·00 | |

*Platinum-salt.* — The solution of the oxide mixed with hydrochloric acid and bichloride of platinum, yields a platinum-salt, which is insoluble in alcohol and ether, but crystallises from water in beautiful octohedra.

| | | | Hofmann & Cahours. |
|---|---|---|---|
| $(C^2H^3)^4P$ | 91·0 | 30·73 | |
| 3 Cl | 106·5 | 35·95 | |
| Pt | 98·7 | 33·32 | 33·30 |
| $(C^2H^3)^4P,HCl + PtCl^2$ | 296·2 | 100·00 | |

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## Nitroform.

$C^3N^3HO^{12} = C^3X^3H.$

L. Schischkoff. *Ann. Pharm.* 103, 364.

*Hydride of Ternitromethyl.*

*Formation and Preparation.* 1. Ternitracetonitryl, $C^4X^3N$, — a product of the action of strong nitric acid on fulminuric acid (x, 556), — treated with water, yields the ammonium-salt of nitroform;

$$C^4X^3N + 2HO = C^3X^3,NH^4 + 2CO^2;$$

and on treating this salt with strong sulphuric acid, sulphate of ammonia is formed, and nitroform rises to the surface, forming a very mobile liquid stratum which solidifies on cooling :

$$C^4X^3,NH^4 + SO^4,H = C^4X^3,H + SO^4,NH^4.$$

The nitroform is then separated by a pipette, and purified by two or three crystallisations, the portion which remains liquid being each time

decanted. — 2. Ternitracetonitryl treated with a strong solution of potash yields a yellow crystalline salt, which when treated with sulphuric acid yields nitroform.

*Properties.* Colourless; solid below 15°. Crystallises in cubes or perhaps in rhombohedrons. Has a very unpleasant odour and bitter taste. It may be preserved without alteration in a cool place.

| | | | | Schischkoff. | | |
|---|---|---|---|---|---|---|
| 2 C | 12 | 7·94 | 9·03 | 7·50 | 7·91 |
| H | 1 | 0·66 | 0·84 | 0·87 | 0·89 |
| 3 N | 42 | 27·81 | 27·05 | 28·00 | |
| 12 O | 96 | 63·59 | | | |
| $C^2HN^3O^{12}$ | 151 | 100·00 | | | |

*Decompositions.* 1. Nitroform is very inflammable, and explodes with violence when quickly heated. It cannot be distilled under the ordinary atmospheric pressure without decomposition, for it decomposes rapidly at 100°, giving off a large quantity of gas, which carries some of the nitroform along with it.

*Combinations.* Nitroform dissolves readily in *water*, forming a dark yellow solution. It possesses acid properties.

Its *salts* are crystallisable, of a fine yellow colour, explode when heated, and sometimes decompose spontaneously, with evolution of gas.

The *ammonium*-salt crystallises well and may be kept unaltered for several days. It gives off a large quantity of ammonia when treated with lime at ordinary temperatures.

## Binitromethylic Acid. $C^2N^2H^4O^4$.

FRANKLAND. *Phil. Trans.* 1857, 59; *Ann. Pharm.* 99, 369; *Chem. Soc. Qu. J.*

*Dinitromethylic acid.*

Formed by the action of binoxide of nitrogen on zinc-methyl. The two bodies gradually unite and form crystalline needles consisting of a compound of binitromethylate of zinc, $C^2H^3ZnN^2O^4$, with zinc-methyl:

$$2C^2H^3Zn + 2NO^2 = C^2H^3ZnN^2O^4,C^2H^3Zn.$$

This compound oxidises rapidly in the air and takes fire when exposed in considerable quantity. It is instantly decomposed by water, yielding marsh-gas and an opalescent solution of basic binitromethylate of zinc:

$$C^2H^3ZnN^2O^4,C^2H^3Zn + HO = C^2H^3ZnN^2O^4,ZnO + C^2H^4.$$

*Normal Zinc-salt,* $C^2H^3ZnN^2O^4 + HO$. — When carbonic acid is passed through the opalescent solution of the basic zinc-salt just mentioned, carbonate of zinc is precipitated, and the liquid, after being boiled and filtered, yields by evaporation crystals of the normal zinc-salt.

| | At 100°. | | Frankland. |
|---|---|---|---|
| 2 C | 12 | 10·30 | 11·28 |
| 2 N | 28 | 24·03 | |
| 4 H | 4 | 3·43 | 3·50 |
| ZnO | 40·5 | 34·77 | 33·86 |
| 4 O | 32 | 27·47 | |
| $C^2H^3ZnN^2O^4,HO$ | 116·5 | 100·00 | |

The excess of carbon in the analysis arises from the passage of nitric oxide into the potash apparatus. In bodies containing so large a proportion of oxidised nitrogen, it is exceedingly difficult to decompose the whole of the nitric oxide by red-hot copper.

*Soda-salt*, $C^2H^3NaN^2O^4 + 2HO$. — Obtained by treating a solution of the zinc-salt with carbonate of soda, evaporating to dryness and exhausting the residue with strong alcohol. The filtered solution yields by evaporation, crystals of the soda-salt containing 25·83 p. c. of soda (by calculation, 25·72). The salt dissolves very readily in water and in alcohol, burns intensely when heated, and in other respects closely resembles the corresponding ethyl-compound.

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## Page 417.

*Cyanide of Barium* is obtained in the pure state by igniting ferrocyanide of barium and potassium (prepared by precipitating 2 pts. of ferrocyanide of potassium with 2 pts. of chloride of barium) in a close vessel, exhausting the residue with water, distilling off the greater part of the liquid, and leaving the remainder to cool: it is somewhat sparingly soluble in water and absorbs carbonic acid quickly from the air. — *Cyanide of Strontium* may be prepared in a similar manner from ferrocyanide of strontium and potassium (obtained by boiling prussian blue with strontia-water); also *cyanide of calcium*, which crystallises in cubes, and *cyanide of magnesium*, which is less easily decomposed by carbonic acid than the preceding salts. (C. Shulz, *J. pr. Chem.* 68, 257.)

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## Page 462.

*Decomposition of Ferrocyanide of Potassium.* — In the preparation of carbonic oxide by heating 1 pt. of finely pulverised ferrocyanide of potassium with 9 pts. of strong sulphuric acid (Fownes's process), the first portions of gas are always contaminated with 11 or 12 per cent. of carbonic and sulphurous acids, but after a while the carbonic oxide is given off pure. When the mixture has been heated to a certain temperature, at which it begins to froth, the evolution of carbonic oxide goes on for a long time by itself; and if the mixture be again heated after the spontaneous evolution of gas has ceased, fresh quantities of gas are obtained, but more or less contaminated with sulphurous acid. — At the beginning of the action, there is formed a white mass like the residue

of the preparation of hydrocyanic acid; but subsequently, this mass dissolves and forms a clear solution, which deposits white nacreous laminæ containing 30·10 p. c. $Fe^2O^3$, 61·70 $SO^3$ and 8·54 KO. The formula $2(Fe^2O^3,3SO^3) + KO,SO^3$ requires 32·8 $Fe^2O^3$, 57·4 $SO^3$, and 9·6 KO. Half an ounce of ferrocyanide of potassium decomposed as above yields about 250 cubic inches of carbonic oxide, which, after passing through potash-ley, may be considered as pure. (Grimm & Ramdohr, *Ann. Pharm.* 98, 127.)

Ferrocyanide of potassium and ammonium $K(NH^4)FeCy^3$, boiled with finely divided peroxide of manganese, gives off ammonia and forms ferricyanide of potassium, probably as represented by the equation

$$2K(NH^4)FeCy^3 + 2MnO^2 = K^2(NH^4)Fe^2Cy^6 + NH^4O + Mn^2O^3.$$

After the boiling has been continued for some time, a green precipitate is formed.

A mixture of ferricyanide of potassium, hydrate of potash, and hydrocyanic acid in equal numbers of atoms, becomes first yellow, then red or nearly black, and forms, with slight evolution of gas, a reddish black precipitate; most quickly when the solution is warm and concentrated; a more dilute solution requires to be heated to the boiling point. The precipitate is nearly insoluble in cold water, but dissolves very easily in alkaline water, and is reprecipitated by acids. It gives off 10·5 p. c. water at 100°. Contains 38·95 to 42·42 p. c. carbon, 41·62 to 42·78 p. c. nitrogen, and 3·2 to 3·4 p. c. hydrogen. A similar product, precipitated by chlorine gas from a solution of cyanide of potassium, yielded by analysis from 35·2 to 36·2 p. c. C, 42·3 N, and 3·0 to 3·1 H. (L. Playfair, *Chem. Soc. Qu. J.* 9, 128.)

# ADDITIONS TO VOL. VIII.

## Page 4.

*Ammoniacal Cuproso-cupric Cyanides.* — *a.* $2NH^3,2Cu^2Cy,CuCy$. — When an ammoniacal solution of hydrated cupric oxide is poured into aqueous hydrocyanic acid, till the odour of ammonia decidedly predominates; the slightly yellow liquid heated to the boiling point; the heat kept up, and the gradual addition of the ammoniacal copper-solution continued till its dark-blue colour no longer disappears,—micaceous crystalline laminæ make their appearance after a while in the liquid. If it be then filtered, it yields on cooling, green rectangular laminæ of remarkable lustre. They have the composition denoted by the above formula, together with 2 At. water. — On heating them with equal volumes of solutions of caustic ammonia and carbonate of ammonia not too dilute, a blue solution is obtained, which, after boiling for an hour, deposits shining blue laminæ consisting of the same compound in the anhydrous state. The green laminæ also turn blue when treated with fixed alkalis or their carbonates, even in the cold.

| *Anhydrous.* | | | Hilkenkamp. | *Hydrated.* | | | Hilkenkamp. |
|---|---|---|---|---|---|---|---|
| $2\ NH^3$ | 34·0 | 12·57 | 12·67 | $2\ NH^3$ | 34·0 | 11·79 | 11·57 |
| 5 Cu | 158·5 | 58·59 | 58·21 | 5 Cu | 158·5 | 54·94 | 54·37 |
| 3 Cy | 78·0 | 28·84 | 28·73 | 3 Cy | 78·0 | 27·04 | 27·30 |
| | | | | 2 HO | 18·0 | 6·23 | 6·76 |
| $2NH^3,2Cu^2Cy,CuCy$ | 270·5 | 100·00 | | + 2Aq | 288·5 | 100·00 | 100·00 |

The compound is quite insoluble in cold water; and is decomposed by boiling water, with formation of a brown substance. Dilute acids separate from it white cuprous cyanide, which dissolves on boiling, with evolution of hydrocyanic acid. (L. Hilkenkamp, *Ann. Pharm.* 97, 218.)

## Page 10.

*Potassio-cuprous Ferrocyanide* $2\mathfrak{C}uKFeCy^3 + 3Aq$.* — When the red-brown precipitate of ferrocyanide of copper ($Cu^2FeCy^3$) produced by adding ferrocyanide of potassium to cupric salts, is heated with solution of cyanide of potassium (obtained by mixing prussic acid and potash), cyanogen is evolved, and a light yellow solution is formed, which, if the cyanide of potassium is not in excess, deposits, first a deep red precipi-

* $\mathfrak{C}u = Cu^2$.

tate and, after this has been separated by filtration, and the liquid left to stand for some time,—small dark red-brown crystals, which, when viewed by the microscope, present the appearance of square prisms. These crystals have the composition indicated by the above formula. The same compound is more easily obtained by dropping a solution of sulphate of copper into a mixture of cyanide and ferrocyanide of potassium, then heating the liquid and leaving it to stand. The crystals give off water at 100° and turn black: they are insoluble in water, ether and alcohol, but soluble in cyanide of potassium. Boiling water decomposes them, with formation of ferrocyanide of potassium. Acids decompose them, separating white cuprous ferrocyanide $Cu^2FeCy$, which when exposed to the air, is immediately converted into cupric ferrocyanide $Cu^2FeCy$.

*Potassio-cupric Ferrocyanide*, $Cu^2FeCy^3 + Aq$. — The above-mentioned dark-red precipitate, obtained in the preparation of the preceding compound, when a comparatively small quantity of cyanide of potassium is used.

The corresponding *sodium*-compounds, $CuKFeCy^3$ and $CuKFeCy^2$, are obtained in like manner with cyanide of sodium. — With cyanide of *ammonium*, a scarlet crystalline body is produced which turns brown in drying, and has the composition $Cu(NH^4)FeCy^3$.

The ferrocyanides of *cobalt* and *nickel* also dissolve in cyanide of potassium, but the solution merely yields separate crystals of ferrocyanide of cobalt or nickel together with ferrocyanide of potassium.

When a dilute solution of 3 At. cupric sulphate and 1 At. ferrous sulphate is mixed with a quantity of ferrocyanide of potassium not sufficient to decompose the whole, and the filtrate consequently still appears bluish, a deep black very bulky precipitate is formed, which is difficult to wash, is altered by contact with the air, and is also deep black when dry and quite destitute of crystalline character. It is insoluble in water, alcohol and dilute acid, and is decomposed by potash, with formation of ferrocyanide of potassium, and separation of protoxide and dioxide of copper; it is not decomposed by oxalic acid. It appears to be a compound analogous to prussian blue. (C. Schulz, *J. pr. Chem.* 68, 257.)

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*Platinocyanides*, $MPtCy^2$. — The *barium-salt* of this series is best obtained, according to Weselsky, by triturating 2 pts. of protochloride of platinum and 3 pts. of carbonate of baryta with water, heating the mixture with 10 pts. of water nearly to the boiling point, and passing vapour of hydrocyanic acid through the liquid as long as carbonic acid continues to escape. — The other platinocyanides may be prepared, either by decomposing the barium-salt with sulphates, or by treating the corresponding carbonates with platino-cyanide of hydrogen (obtained by decomposing the barium-salt with sulphuric acid). — A yellow *platinocyanide of magnesium*, $MgPtCy^2 + 6HO$ (also observed by Schafarik, x, 509) is obtained by leaving a solution of the ordinary red and metal-green magnesium-salt (viii, 254) in hot water or in absolute alcohol, to crystallise over oil of vitriol. Lemon-yellow plates are then deposited, a line

in width, several lines in length, and exhibiting a blue iridescence by reflected light. — A red *platino-cyanide of hydrogen* $HPtCy^2 + 5HO$ (also observed by Quadrat) is obtained by treating platinocyanide of barium or potassium with an equivalent quantity of strong sulphuric acid, digesting in a mixture of ether and alcohol, and drying over sulphuric acid. The hydrogen-salt is then deposited in crystals 7 or 8 lines in length, half a line thick, and having a splendid vermilion colour with blue iridescence on the prismatic faces. The crystals absorb water from the air and then assume the ordinary appearance of hydroplatinocyanic acid. (Weselsky, *J. pr. Chem.* 69, 276.)

*Platinosesquicyanides*, $M^2Pt^2Cy^5$ or $2MCy,Pt^2Cy^3$. — These compounds are obtained by triturating the platinocyanides with nitric acid of sp. gr. 1·3, removing the excess of nitric acid by draining and pressure, and recrystallising several times from the smallest possible quantity of cold water:

$$3MPtCy^2 + 2NO^5 = M^2Pt^2Cy^5 + MO,NO^5 + PtCy + NO^4.$$

They are all soluble in water and alcohol, and all form colourless solutions, excepting the lithium-salt, which is yellowish. — The *potassium-salt* $K^2Pt^2Cy^5 + 6HO$ (also observed by Knop, viii, 49) crystallises in slender undefined needles having a coppery metallic lustre but appearing green by transmitted light. They turn dark green at 180°, and yellow at 200°, without losing their metallic lustre. — The *ammonium-salt* $(NH^4)^2Pt^2Cy^5$ crystallises in thin needles often half an inch long. It has a golden yellow metallic lustre, becomes steel-green at 150°, with partial decomposition, and lemon yellow between 180° and 190°. It is more soluble in water than the potassium-salt. — The *lithium-salt* $Li^2Pt^2Cy^5 + 6HO$ is still more soluble both in water and in alcohol. — The *magnesium-salt* forms a blackish violet satiny mass of microscopic needles. (Weselsky.)

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*Ferrous Sulphocyanide* $FeCyS^2 + 3HO$. — When a solution of iron wire in hydro-sulphocyanic acid concentrated as much as possible, is left to evaporate in vacuo over oil of vitriol, ferrous sulphocyanide is deposited in rather large oblique rhombic prisms having an intense green colour, and a bitter inky taste. They dissolve readily in water, alcohol and ether. Both the crystals and their solution quickly turn red on exposure to the air. The crystals are decomposed by heat, with evolution of sulphide of carbon and formation of mellonide of iron.

| | | | | Claus. |
|---|---|---|---|---|
| | Fe | 28·0 | 23·83 | 23·56 |
| 2 | S | 32·0 | 27·23 | 27·44 |
| | Cy | 26·0 | 22·12 | |
| 3½ | HO | 31·5 | 26·82 | 26·74 |
| | $FeCyS^2 + 3\frac{1}{2}Aq$? | 117·5 | 100·00 | |

Most probably the salt was imperfectly dried, and the proper quantity of water is 5 At.

*Ferric Sulphocyanide* $Fe^2(CyS^2)^3+3HO$. — 1. Remains in the form of a dark brown-red, nearly black, crystalline mass when a solution of recently precipitated ferric hydrate in concentrated hydrosulphocyanic acid is left to evaporate over oil of vitriol. — 2. By digesting a mixture of 2 At. anhydrous ferric sulphate and 1 At. sulphocyanide of potassium with alcohol, and evaporating the solution over oil of vitriol, the salt is obtained in small dark red crystals of cubic form but not well defined.

| | | | | Claus. |
|---|---|---|---|---|
| 2 Fe | 56 | .... | 21·79 | 21·91 |
| 6 S | 96 | .... | 37·35 | 37·37 |
| 3 Cy | 78 | .... | 30·35 | |
| 3 HO | 27 | .... | 10·51 | 11·00 |
| $Fe^2,(CyS^2)^3 + 3Aq$ | 257 | .... | 100 00 | |

The salt decomposes after keeping for some time, and exhibits when heated the same behaviour as ferrous sulphocyanide. Its concentrated aqueous solution is decomposed, like cupric sulphocyanide, by dilution with a large quantity of water (but not with alcohol), losing its colour, and depositing a light yellow substance, which is probably a basic compound of ferric oxide with a product of the decomposition of sulphocyanogen. The coloured filtrate contains hydrocyanic and sulphuric acids, together with a small quantity of free hydrosulphocyanic acid, but its principal constituent is ferric sulphocyanide. Nevertheless, the formation of ferric sulphocyanide is the most delicate of all tests for the presence of ferric oxide, provided the liquid is acidulated with hydrochloric acid. In a liquid containing only $\frac{1}{1,000,000}$ part of iron in the form of sesquioxide, the reaction is still perceptible, provided the observer looks down the tube held over a white surface; $\frac{1}{500,000}$ of iron gives a deep rose colour. The red solution is decolorised by polybasic organic acids and likewise by phosphoric acid.

Ferric sulphocyanide dissolves readily in *water*, *alcohol* and *ether*. Ether extracts it from its aqueous solution, producing a violet-purple-red liquid which is reduced by light to green ferrous sulphocyanide. (Claus.)

*Sulphocyanide of Cobalt*, $CoCyS^2$, forms prisms of a fine deep violet colour. (Claus, *Ann. Pharm* 99, 48.)

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*Sulphocyanide of Silver.* — When a moderately concentrated solution of sulphocyanide of silver and ammonium (or potassium) is mixed with aqueous ammonia, the liquid gradually becomes filled with colourless nacreous laminæ of sulphocyanide of silver. When a lump of the double salt evaporated to dryness is immersed in dilute ammonia, the compound changes for a while to an amorphous mass resembling chloride of silver, and a few seconds after, the vessel becomes filled with a most beautiful crystalline magma. Hydrochloric acid acts like ammonia. Sulphocyanide of silver and ammonium is completely decomposed by water, with separation of granular sulphocyanide of silver. [A similar decomposition of the potassium salt was observed by Hull (viii, 97.)]

—Recently precipitated oxide of silver digested at a gentle heat in sulphocyanide of ammonium, gradually dissolves, with evolution of ammonia. The liquid, which always contains an excess of sulphocyanide of ammonium, likewise deposits crystallised sulphocyanide of silver on addition of ammonia or hydrochloric acid.

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## Hydrate of Ethylene.

$$C^4H^6O^4 = \left.\begin{matrix}C^4H^4\\H^2\end{matrix}\right\}O^4.$$

A. Wurtz. *Compt. rend.* 43, 199; *Ann. Pharm.* 100, 110.

*Glycol.*

*Formation and Preparation.* By the action of hydrate of potash on acetate of ethylene:

$$\left.\begin{matrix}C^4H^4\\(C^4H^3O^2)^2\end{matrix}\right\}O^4 + 2KHO^2 = \left.\begin{matrix}C^4H^4\\H^2\end{matrix}\right\}O^4 + 2\left(\left.\begin{matrix}C^4H^3O^2\\K\end{matrix}\right\}O^2\right)$$

*Preparation.* Acetate of ethylene (6·15 grm.) is mixed in a flask with hydrate of potash, (4·72 grm.) previously ignited and pulverised. A brisk action immediately takes place, and after the lapse of a day, a mass of acetate of potash is found in the flask. The mixture is then heated to 180° in an oil-bath, and after a small distillation-tube has been adapted to the flask, the heat is raised to between 250° and 260°. A colourless liquid then passes over, which is to be rectified, and the portion which distils between 190° and 200° collected apart.

*Properties.* Colourless, somewhat viscid liquid, having a sweet taste. Boils at 195° and distils without decomposition. Its vapour is inflammable.

| | | | Wurtz. |
|---|---|---|---|
| 4 C | 24 | 38·7 | 38·7 |
| 6 H | 6 | 9·7 | 9·9 |
| 4 O | 32 | 51·6 | 51·4 |
| $C^4H^6O^4$ | 62 | 100·0 | 100·0 |

May be regarded as a double molecule of water $\left.\begin{matrix}H^2\\H^2\end{matrix}\right\}O^4$, in which 2 At. H are replaced by the biatomic radical $C^4H^4$ (compare page 222 of this volume).

*Decompositions.* 1. Hydrate of ethylene is converted by oxidation with nitric acid, into glycolic acid $C^4H^4O^6$, and afterwards into oxalic and carbonic acids. When it is dissolved in four times its volume of nitric acid, of sp. gr. 1·33 and solution is left to evaporate for several days over caustic lime in vacuo at the temperature of the air, a syrupy liquid remains, which, when diluted with water, neutralised with

chalk, and treated with alcohol after filtration, yields a precipitate of glycolate of lime $C^4H^3CuO^6$. — The alcoholic liquid filtered from this precipitate does not contain any substance capable, like aldehyde, of uniting with bisulphite of soda. — Boiled for some minutes with four times its volume of weak nitric acid, it gives off red vapours, and the solution on cooling solidifies in a pulpy mass consisting of interlaced crystals of oxalic acid. — Monohydrated nitric acid acts still more violently, carbonic acid being evolved, and glycolic and oxalic acids remaining in solution. — 2. Pure hydrate of ethylene dropped on platinum-black makes it red-hot and gives off carbonic acid. A solution of hydrate of ethylene in four times its bulk of water, added to platinum-black, also causes rise of temperature and evolution of carbonic acid, and the platinum-black is afterwards found to contain traces of glycolic acid. Wurtz (*Ann. Pharm.* 103, 366.)

*Combinations.* Hydrate of ethylene is soluble in all proportions in *water* and in *alcohol*.

## Acetate of Ethylene.

$$C^{12}H^{10}O^8 = \left.\begin{matrix} C^4H^4 \\ (C^4H^3O^2)^2 \end{matrix}\right\} O^4.$$

A. Wurtz. *Compt. rend.* 43, 199; *Ann. Pharm.* 100, 110.

*Acetate of Glycol.*

*Formation.* By the action of iodide of ethylene on acetate of silver:

$$C^4H^4I^2 + 2\left(\left.\begin{matrix} C^4H^3O^2 \\ Ag \end{matrix}\right\} O^2\right) = \left.\begin{matrix} C^4H^4 \\ (C^4H^3O^2)^2 \end{matrix}\right\} O^4 + 2AgI.$$

*Preparation.* Iodide of ethyl is mixed by small portions with well dried actate of silver (10 grm. of the former to 12 grm. of the latter; it is not advisable to operate with larger quantities), and the mixture is introduced into a flask. A brisk action soon begins, and the mass assumes a yellow colour from formation of iodide of silver, and gives off a considerable quantity of gas, principally carbonic acid and olefiant gases (arising from secondary actions). As soon as the mixture is sufficiently cooled, a fresh portion is introduced, and the process continued till between 100° and 150° grammes of iodide of ethylene have been used. At the end of the reaction, there is found in the flask, a yellow mass of iodide of silver, saturated with a liquid; and on distilling this mixture, which requires a somewhat high temperature, an acid liquid passes over, coloured brown by iodine and containing acetic acid besides neutral products. When subjected to fractional distillation, it begins to boil at 120°, but the temperature soon rises, and the portion which distils over between 160° and 200°, must be collected apart. The distillate, which is still acid, is redistilled over oxide of lead, and again subjected to fractional distillation, till it passes over almost entirely between 180° and 190°. If it still contains a trace of iodide, it must be rectified over oxide of silver.

*Properties.* Colourless neutral liquid, nearly inodorous at ordinary temperatures but smelling slightly of acetic acid when heated. It is heavier than water and sinks to the bottom of it in large drops. Boils at 185°, and distils without decomposition.

| Calculation. | | | | | Vol. | | Density. |
|---|---|---|---|---|---|---|---|
| 12 C | 72 | .... | 49·31 | C-vapour | 12 | ..... | 4·9920 |
| 10 H | 10 | .... | 6·85 | H-gas | 10 | ..... | 0·6930 |
| 8 O | 64 | .... | 43·84 | O-gas | 4 | ..... | 4·4372 |
| $C^{12}H^{10}O^8$ | 146 | .... | 100·00 | Vapour of $C^{12}H^{10}O^8$ | 2 | ..... | 10·1222 |
| | | | | | 1 | ..... | 5·0611 |

$$= \underbrace{2C^4H^4O^4}_{\text{acetic acid.}} + \underbrace{C^4H^6O^4}_{\text{glycol.}} - 4HO.$$

By bases, *e. g.* potash or baryta, in presence of water, it is resolved into acetic acid and hydrate of ethylene, (p. 501). 1·298 grm. acetate of ethylene was heated with excess of hydrate of baryta to between 120° and 130° in a sealed tube, and the product was diluted with water, saturated with carbonic acid and filtered. The filtrate contained acetate of baryta, which, when decomposed by sulphuric acid, yielded 1·850 grm. sulphate of baryta: or 1 At. acetate of ethylene, yielded 1·8 At., or nearly 2 At. acetic acid.

Acetate of ethylene dissolves in a very large quantity of *water*, and is also soluble in alcohol.

*Ethyl-glycerine*, $C^4H^6O^6 = \left.\begin{matrix}C^4H^3\\H^3\end{matrix}\right\}O^3$. In the preparation of acetate of ethylene above described, there is also formed an oily liquid which remains in the retort after the acetate of ethylene has passed over, and has a boiling point above 250°. This liquid appears to be the acetate of ethyl-glycerine, a compound homologous with triacetin (ix, 497), and containing $C^4H^3$ in place of $C^6H^5$.

## Glyoxal. $C^4H^2O^4$.

DEBUS. *Ann. Pharm.* 102, 20.

*Formation* (p. 506).

*Preparation.* When the syrupy neutral liquid obtained in the preparation of glyoxylic acid, is mixed with several times its volume of a concentrated solution of bisulphite of ammonia, and the mixture left to itself for some hours, the sides of the vessel become covered with a white crystalline crust consisting of a compound of glyoxal with bisulphite of soda; and by dissolving this product in the smallest possible quantity of boiling water and leaving the filtrate to cool quietly, the compound is deposited in fine crystals, which, after two crystallisations, are obtained quite pure. A further quantity may be obtained by treating the mother-liquors with alcohol. The sodium-compound mixed with chloride of barium yields, after two days, crystals of the corresponding barium-compound, which may also be purified by recrystallisation, and by decomposing the barium-compound with the exact quantity of sulphuric acid required, and evaporating the filtrate to remove water and sulphurous acid, glyoxal is obtained in the solid state.

*Properties.* Transparent, slightly yellowish, amorphous mass, which deliquesces when exposed to the air.

| | *At* 100°. | | Debus. |
|---|---|---|---|
| 4 C | 24 | 41·37 | 40·2 |
| 2 H | 2 | 3·45 | 3·5 |
| 4 O | 32 | 55·18 | 56·3 |
| $C^4H^2O^4$ | 58 | 100·00 | 100·0 |

The deficiency of carbon in the analysis is due to an admixture of the barium-compound, which could not be completely removed.

Glyoxal may be regarded as the aldehyde of glyoxylic acid ($C^4H^2O^6$). It stands between glycol and oxalic acid, in the same manner as ordinary aldehyde between alcohol and oxalic acid. Common alcohol (monatomic) by losing 2 At. H, is converted into aldehyde, and aldehyde, by taking up 2 O, is converted into acetic acid. In like manner, glycol, which is biatomic, by giving up 4 At. H, becomes glyoxal, and glyoxal, by taking up 4 At. O, is converted into oxalic acid $C^4H^2O^8$.

*Decompositions.* 1. An aqueous solution of glyoxal treated with a small quantity of very dilute nitric acid and evaporated over the water-bath, leaves a residue of glyoxylic acid. An excess of nitric acid, even when very dilute, converts it into oxalic acid. — 2. Glyoxal is decomposed by sulphuretted hydrogen. — 3. By caustic alkalis, even at ordinary temperatures, it is converted into a salt of glycolic acid : *e.g.*

$$C^4H^2O^4 + CaO,HO = \underbrace{C^4H^3CaO^6}_{\text{glycolate of lime.}}$$

4. The aqueous solution is merely clouded by neutral acetate of lead, but, on addition of ammonia, a copious white precipitate is formed. — With nitrate of silver and ammonia, it forms a beautiful speculum of silver.

*Combinations.* Glyoxal dissolves very readily in water.

*Glyoxal with Ammonia.* — Ammoniacal gas passed through an ethereal solution of glyoxal forms a white precipitate.

*Glyoxal with Bisulphite of Ammonia.* — A concentrated solution of bisulphite of ammonia mixed with glyoxal deposits this compound in crystals, the deposition of which is attended with considerable evolution of heat. The crystals are purified by recrystallisation from hot water, but the boiling must not be long continued, as otherwise, a portion of the salt is apt to decompose.

Shining prismatic crystals, white, or often slightly yellowish; very soluble in water, insoluble in alcohol. The aqueous solution is precipitated by acetate of lead, but not by salts of zinc, copper or silver.

| | *Dried in vacuo.* | | Debus. |
|---|---|---|---|
| 4 C | 24 | 10·0 | 10·0 |
| 10 H | 10 | 4·2 | 4·5 |
| 2 N | 28 | 11·8 | |
| 6 O | 48 | 20·3 | |
| 4 $SO^2$ | 128 | 53·7 | 52·8 |
| $C^4(NH^4)^2O^4,4SO^2 + 2Aq$ | 238 | 100·0 | |

*Glyoxal with Bisulphite of Soda.* — *Preparation* (p. 503). Small hard white crystals, easily soluble in water, insoluble in alcohol. The aqueous solution, when boiled for some time, acquires a slight yellowish tint; it precipitates acetate of lead and chloride of barium. It is slowly decomposed by hydrochloric and sulphuric acids, with evolution of sulphurous acid; also by hot nitric acid, with formation of oxalic and sulphuric acids. With caustic soda and carbonate of soda, it turns brown and forms a dark-coloured precipitate. When glyoxal is mixed, first with caustic soda, and then with sulphite of soda, the mixture remains colourless, because the glycolate of soda formed by the action of the caustic soda is not affected by sulphites.

| *Dried in vacuo.* | | | Debus. |
|---|---|---|---|
| 4 C | 24 | 8·45 | 8·44 |
| 6 H | 6 | 2·11 | 2·16 |
| 2 Na | 46 | 16·19 | 16·06 |
| 10 O | 80 | 28·16 | 27·94 |
| 4 $SO^2$ | 128 | 45·09 | 45·40 |
| $C^4H^2O^4,2(NaO,HO,2SO^2) + 2Aq$.. | 284 | 100·00 | 100·00 |

*Glyoxal with Bisulphite of Baryta.* — *Preparation* (p. 503). The hot-saturated solution deposits after about two days, nearly the whole of the salt in indistinct concentrically grouped masses.

| *Dried in vacuo.* | | | Debus. |
|---|---|---|---|
| 4 C | 24 | 5·97 | 6·12 |
| 9 H | 9 | 2·25 | 2·19 |
| 2 Ba | 137 | 34·07 | 33·83 |
| 13 O | 104 | 25·87 | 26·33 |
| 4 $SO^2$ | 128 | 31·84 | 31·53 |
| $C^4H^2O^4,2(BaO,HO,2SO^2) + 5HO$.. | 402 | 100·00 | 100·00 |

The salt heated on platinum foil, blackens, gives off sulphurous acid, and burns away, leaving sulphate of baryta. The aqueous solution boiled with a slight excess of caustic baryta, yields a precipitate of neutral sulphite of baryta, while free baryta and glycolate of baryta remain in the liquid.

$$C^4H^2O^4,2(BaO,HO,2SO^2),5HO + (BaO,HO) = 4(BaO,SO^2) + 9HO + \underbrace{C^4H^3BaO^6}_{\text{glycolate of baryta.}}$$

Glyoxal dissolves with great facility in *alcohol* and *ether*.

## Glyoxylic Acid.

$$C^4H^4O^8 = C^4H^2O^6 + 2HO.?$$

Debus. *Phil. Mag.* [4], 12, 361; *Ann. Pharm.* 100, 1.

*Formation.* By the action of nitric acid on alcohol:

$$C^4H^6O^2 + 8O = C^4H^2O^6 + 4HO \text{ or } C^4H^4O^8 + 2HO.$$

Debus originally regarded glyoxylic acid as $C^4H^4O^6$ (its salts having indeed the composition $C^4H^3MO^8$), and supposed that it was produced by the oxidation of glycolic acid $C^4H^4O^6$, that compound being previously formed by the action of the nitric acid on the alcohol; but he now (*Ann. Pharm.* 102, 28) rather regards it as $C^4H^2O^6$ (glyoxal, $C^4H^2O^4$, being the corresponding aldehyde), and supposes its formation from alcohol to be preceded by that of glycol and glyoxal, according to the equations:

$$C^4H^6O^2 + O^2 = \underbrace{C^4H^6O^4}_{\text{glycol.}}$$

$$\underbrace{C^4H^6O^4}_{\text{glycol.}} + 4O = \underbrace{C^4H^2O^4}_{\text{glyoxal.}} + 4HO.$$

and:

$$\underbrace{C^4H^2O^4}_{\text{glyoxal.}} + 2O = \underbrace{C^4H^2O^6}_{\text{glyoxylic acid.}}$$

This supposition does not indeed agree with the composition of the glyoxylates, which in the anhydrous state appear to be $C^4H^3MO^8$; but Debus suggests that there may be an anhydrous glyoxylic acid $C^4H^2O^6$, related to glyoxylic acid $C^4H^4O^8$, in the same manner as anhydrous tartaric acid (x, 336) to ordinary tartaric acid, and containing hydrogen replaceable by metals.

*Preparation.* 220 grms. of 80 per cent. alcohol are poured into a tall narrow flask capable of holding about 1½ lb. of water; 100 grammes of water are introduced below the alcohol by means of a funnel having its neck finely drawn out; and below this, are poured 200 grms. of red fuming nitric acid, so that the three liquids may remain one above the other and mix as little as possible at first. The bottle is then closed with a cork fitted with a gas-delivery tube dipping under water, and the whole is left for six or eight days, at a temperature of 20° to 22°, till the liquids have become completely mixed, and the resulting nitrite of ethyl has volatilised. The residual liquid, containing nitric, acetic and formic acids, compound ethers, glyoxal and other aldehydes, glycolic acid and glyoxylic acid, is evaporated to a syrup over the water-bath in portions of 20 to 30 grms. each; the residues containing oxalic, glycolic and glyoxylic acids, together with the less volatile aldehydes, are dissolved in small quantities of water; the united solutions are neutralised with chalk; the neutral liquid is mixed with an equal volume of alcohol; and the resulting precipitate of lime-salts pressed and repeatedly boiled with water. The supernatant liquid contains glyoxal and glycolate of lime. The aqueous extract yields crystals of glyoxylate of lime, and a further quantity of this salt may be obtained by concentrating the mother-liquor. The subsequent mother-liquors yield a double salt of glycolate and glyoxylate of lime, and the last contain glycolate of lime (p. 509).

The hydrated acid is obtained by decomposing the lime-salt with oxalic acid, and evaporating the solution in vacuo, in the form of a viscid, transparent, slightly yellowish syrup, which dissolves readily in water. The solution heated to 100° gives off unaltered glyoxylic acid together with the watery vapours. The syrupy acid, when strongly heated, gives off acid vapours and volatilises, leaving a scanty black residue.

The *Glyoxylates* $C^4H^3MO^8$, are obtained by neutralising the bases or their carbonates with the aqueous acid.

*Gloxylate of Ammonia* crystallises in hard crusts, consisting of needle-shaped crystals concentrically grouped.

*Glyoxylate of Potash.* — White, very deliquescent salt, difficult to crystallise.

*Glyoxylate of Lime.* — (*Preparation* p. 506). — Crystallises in thin needles or hard prismatic crystals, soluble in 177 pts. of water at 8°.

| | *Dried in vacuo.* | | Debus (*mean*). |
|---|---|---|---|
| 4 C | 24 | 21·62 | 21·62 |
| 3 H | 3 | 2·70 | 2·76 |
| Ca | 20 | 18·01 | 18·20 |
| 8 O | 64 | 57·67 | 57·42 |
| $C^4H^3CaO^8$ | 111 | 100·00 | 100 00 |

The salt may be heated to between 160° and 170° without loss of weight, but is decomposed at 180°, with evolution of water and carbonic acid, and formation of oxalate, glycolate and carbonate of lime, together with a resinous substance. From this decomposition it appears most probable that the salt is anhydrous, and consequently that the formula of glyoxylic acid is $C^4H^4O^8$; it is possible however that it may contain 2 At. water, which are given off only at the temperature at which the salt itself decomposes. In that case the formula of the lime-salt would be $C^4HCaO^6 + 2Aq$ and that of glyoxylic acid $C^4H^2O^6$ (p. 506). The relation of glyoxylic acid to glyoxal is in favour of this supposition.

The solution of glyoxylate of lime mixed with lime-water yields a white precipitate of a basic salt, which is decomposed by carbonic acid in the cold, into carbonate of lime and the neutral glyoxylate; and is resolved by water, gradually at ordinary temperatures, quickly on boiling, into oxalate and glycolate of lime:

$$2C^4H^3CaO^8 + CaO,HO = C^4Ca^2O^8 + C^4H^3CaO^6 + 4HO.$$

The solution of the neutral lime-salt is not precipitated by nitrate of baryta or chloride of copper.

*Glyoxylate of Lead.* — White precipitate obtained by adding neutral acetate of lead to the aqueous solution of the lime-salt.

| | | | Debus. |
|---|---|---|---|
| 4 C | 24·0 | 8·0 | 7·6 |
| 2 H | 2·0 | 0·7 | 1·1 |
| 2 Pb | 207·6 | 69·7 | 70·9 |
| 8 O | 64·0 | 21·6 | 20·4 |
| $C^4H^2Pb^2O^8$ | 297·6 | 100·0 | 100·0 |

The composition of this salt seems to show that the acid is bibasic; the formation of a basic lime-salt tends towards the same conclusion, which is also in accordance with the relation of glyoxylic acid to glycol and glyoxal. If glyoxylic acid be really $C^4H^2O^6$, the three compounds, glycol $C^4H^6O^4$, glyoxylal $C^4H^2O^4$, and glyoxylic acid $C^4H^2O^6$, will be related to each other in the same manner as alcohol, aldehyde and acetic acid.

*Glyoxylate of Silver.* — Oxide of silver dissolves in aqueous glyoxylic acid, and the concentrated solution left to evaporate at ordinary temperatures, yields white rhombic crystals, which however are always contaminated with metallic silver, even if the light has been carefully excluded. The aqueous solution deposits a silver speculum when boiled.

## Glycolic Acid.

$C^4H^4O^6 = C^4H^4O^2,O^4$.

SOCOLOFF & STRECKER. (1851.) *Ann. Pharm.* 80, 18.
DESSAIGNES. *Compt. rend.* 38, 44.

*Formation and Preparation.* 1. Benzoglycolic acid (p. 66) is resolved by boiling with water to which a little sulphuric acid is added, into glycolic and benzoic acids: the greater part is decomposed in the course of a few hours, but to render the decomposition quite complete, several days boiling is required. The liquid is evaporated as long as benzoic acid continues to separate on cooling, then neutralised with carbonate of baryta, filtered from the resulting sulphate of baryta, and evaporated to a syrup. The baryta-salt which crystallises out on cooling, is dissolved in a small quantity of water, and decomposed by dilute sulphuric acid; the filtered solution evaporated to a syrup; this residue dissolved in ether; and the ethereal solution left to evaporate. (Socoloff & Strecker.)

2. An aqueous solution of glycocol is decomposed by nitrous acid with evolution of nitrogen gas; the liquid with shaken up ether and evaporated leaves glycolic acid:

$$C^4NH^5O^4 + NO^3 = C^4H^4O^6 + HO + 2N.$$

If the liquid is evaporated immediately after the action of the nitrous acid, the glycolic acid thus produced is converted into oxalic acid. (Socoloff & Strecker.) Dessaignes, by the same process, obtained glycolic acid in the crystalline form.

3. Tartronic acid (x, 345), is heated to 180°, till no more gas is evolved; the residue consisting of nearly pure glycolide is washed with cold water and dissolved in potash; the resulting glycolate of potash is precipitated by nitrate of silver, and the glycolic acid is separated from the silver-salt by hydrochloric acid. The solution of the acid crystallises in vacuo. (Dessaignes.)

4. When glycol is dissolved in four times its bulk of nitric acid of sp. gr. 1·33; and the solution, after standing for several days, is concentrated in vacuo over quick lime, an acid syrupy residue is left, which when dissolved in water, neutralised with chalk, and mixed with alcohol, yields a precipitate of glycolate of lime; and on precipitating the lime by the exact quantity of oxalic acid required, and evaporating the filtrate in vacuo, glycolic acid is obtained in crystals. (Wurtz, *Compt. rend.* 44, 1306; *Ann. Pharm.* 102, 366.)

Glycolic acid is also produced in the oxidation of alcohol by nitric acid, the intermediate products being glycol and glyoxal. (Debus, p. 506). — Cloez (*Compt. rend.* 34, 364) found in the mother-liquor obtained in the preparation of fulminating mercury, an acid having the composition of glycolic acid. The mother-liquor, after being neutralised with chalk, was distilled in the water-bath, and the residue left after the more volatile products, aldehyde, acetic ether, formic ether, and nitrous ether had passed over, was found to contain nitrate, acetate and formiate of lime, together with the lime-salt of an acid having the composition $C^4H^4O^6$. By repeatedly abandoning the solution to spontaneous evaporation and decanting the liquid containing the more soluble salts, this lime-salt was obtained in small light nodules resembling lactate of

lime; and by decomposing the lime-salt with oxalic acid, and concentrating the solution over the water-bath or in vacuo over oil of vitriol, the acid was obtained in the form of a syrupy liquid resembling lactic acid. Cloez gave to this acid the name *Homolactic acid.*

6. By the action of alkalis on glyoxal or glyoxylic acid. (Debus, pp. 501, 507).

*Properties.* Flat crystals, having the form of laminæ striated on the surface. (Dessaignes.) The *homolactic* acid obtained by Cloez, formed, when concentrated as much as possible, a colourless inodorous syrup, of sp. gr. 1·197 at 13°. Wurtz suggests that glycolic acid may exist in two isomeric modifications.

| | | | Dessaignes. |
|---|---|---|---|
| 4 C | 24 | 31·58 | 31·64 |
| 4 H | 4 | 5·26 | 5·27 |
| 6 O | 48 | 63·16 | 63·09 |
| $C^4H^4O^6$ | 76 | 100·00 | 100·00 |

From the second mode of formation, it appears that glycocol is the amide of glycolic acid: $C^4NH^5O^4 = C^4AdH^3O^2,O^2$ (ix, 247). The peculiar acid which Horsford obtained (ix, 250) by the action of chlorine on glycocol is different from glycolic acid, inasmuch as its ammonia-salt is precipitated by chloride of barium. (Socoloff & Strecker.)

*Combinations.* Glycolic acid dissolves in *water* in all proportions.

The *Glycolates* are for the most part easily soluble in water and crystallisable.

*Glycolate of Baryta.* — *Preparation* p. 508. — Melts when heated, forming a perfectly clear liquid which crystallises on cooling. When strongly heated, it swells up, diffusing a peculiar odour, and leaving nearly colourless carbonate of baryta.

| | | | Socoloff & Strecker. |
|---|---|---|---|
| BaO | 76·6 | 53·34 | 52·70 |
| 4 C | 24·0 | 16·71 | 16·82 |
| 3 H | 3·0 | 2·09 | 2·27 |
| 5 O | 40·0 | 27·86 | 28·21 |
| $C^4H^3BaO^6$ | 143·6 | 100·00 | 100·00 |

*Glycolate of Lime.* — The liquid obtained by the action of nitric acid on glycol yields, when neutralised with chalk and mixed with alcohol, a precipitate, which, when recrystallised from water forms tufts and nodules of delicate interlaced needles. (Wurtz.) — Glyoxal boiled for a few minutes with milk of lime forms a liquid which filtered and freed from excess of lime by carbonic acid, yields glycolate of lime to the last drop. — Glycolate of lime is also found in the mother-liquors obtained in the preparation of glyoxylic acid (p. 506). — The air-dried salt contains 22 p. c. (3 At.) water which it gives off at 100° or a little above. (Wurtz, Debus.)

| | *At* 120°. | | Wurtz. | |
|---|---|---|---|---|
| CaO | 28 | 29·47 | 29·47 | |
| 4 C | 24 | 25·26 | 24·87 | 25·00 |
| 3 H | 3 | 3·15 | 3·52 | 3·40 |
| 5 O | 40 | 42·12 | 42·14 | |
| $C^4H^3CaO^6$ | 95 | 100·00 | 100·00 | |

| | *Dried over oil of vitriol.* | | Debus. |
|---|---|---|---|
| CaO | 28 | 22·95 | 22·68 |
| 4 C | 24 | 19·67 | |
| 3 H | 3 | 2·46 | |
| 5 O | 40 | 32·79 | |
| 3 HO | 27 | 22·13 | 22·10 |
| $C^4H^3CaO^6 + 3Aq$ | 122 | 100·00 | |

Debus' salt was obtained by the action of lime-water on glyoxylate of lime (p. 507).

*Glycolate of Lime with Glyoxylate of Lime.* — Crystallises from the mother-liquors obtained in the preparation of glyoxylic acid (p. 506). It is very soluble in water, and the warm-saturated solution solidifies on cooling to a jelly which, after some days, changes to a crystalline powder. After drying in the air, it gives off 7·71 p. c. water (3 At.; calc. 7·45 p. c.) at 120°, still retaining 2 At. The solution gives with nitrate of baryta, lime-water, chloride of copper, and nitrate of silver, the same reactions as that of glyoxylate of lime (p. 507).

| | *At* 120°. | | Debus. |
|---|---|---|---|
| 12 C | 72 | 21·49 | 21·92 |
| 11 H | 11 | 3·28 | 3·60 |
| 3 Ca | 60 | 17·91 | 18·00 |
| 24 O | 192 | 57·32 | 56·48 |
| $C^4H^3CaO^6,2C^4H^3CaO^6 + 2Aq.$ | 335 | 100·00 | 100·00 |

*Glycolate of Zinc.* — The aqueous acid saturated at the boiling heat with carbonate of zinc, deposits on cooling, crystalline crusts resembling lactate of zinc, or colourless opaque prisms arranged in stellate groups. — The salt is sparingly soluble in cold water, soluble in 33 pts. of hot water, insoluble in alcohol. It gives off 14·35 p. c. (2 At.) water at 100°. (Socoloff & Strecker.)

| | *At* 100°. | | Socoloff & Strecker. |
|---|---|---|---|
| ZnO | 40·5 | 37·67 | 37·64 |
| 4 C | 24·0 | 22·33 | 22·69 |
| 3 H | 3·0 | 2·79 | 3·00 |
| 5 O | 40·0 | 37·21 | 36·67 |
| $C^4H^3ZnO^6$ | 107·5 | 100·00 | 100·00 |

*Glycolate of Silver.* — A solution of glycolide in potash forms with nitrate of silver, a white flocculent precipitate which soon becomes crystalline, dissolves readily in hot water, and may be obtained therefrom in large crystals. At 100° it turns reddish and gives off 4·79 p. c. (1 At.) water. (Dessaignes.) — Glycolate of silver prepared by decomposing glycolate of baryta with sulphate of silver decomposed even while still in solution, the liquid depositing black flakes. The solution likewise turned black when evaporated in vacuo over oil of vitriol, and the viscid residue was no longer completely soluble in water. The aqueous solution of the salt was not precipitated by alcohol or ether. (Strecker.) — Dessaignes neutralised the acid prepared by 2, mixed the solution with nitrate of silver, filtered to separate the reduced silver, and obtained the acid in the crystalline form from the filtrate.

| | Crystallised. | | Dessaignes. |
|---|---|---|---|
| AgO | 116 | 56·25 | 56·12 |
| 4 C | 24 | 12·50 | 12·70 |
| 4 H | 4 | 2·08 | 2·20 |
| 6 O | 48 | 29·17 | 28·98 |
| $C^4H^3AgO^6$ + Aq | 192 | 100·00 | 100·00 |

Glycolic acid mixes in all proportions with *alcohol* and *ether*.

## Glycolamide. $C^4NH^5O^4$.

DESSAIGNES. (1853.) *Compt. rend.* 38, 47.

*Formation and Preparation.* 1. Glycolide is dissolved in hot ammonia. — 2. Tartronate of ammonia melts at 150°, with violent evolution of carbonic acid; after a while however the escape of gas becomes less rapid, and the residue forms on cooling a thick deliquescent syrup (probably glycolate of ammonia). If the heat be continued, carbonate of ammonia escapes, and at last there remains a residue which solidifies on cooling, and when recrystallised yields beautiful crystals of glycolamide. — This compound dissolves readily in water, sparingly in alcohol. Has a faint, somewhat sweetish taste and a slight acid reaction.

| | | | Dessaignes. |
|---|---|---|---|
| 4 C | 24 | 32·00 | 32·10 |
| N | 14 | 18·66 | 18·29 |
| 5 H | 5 | 6·66 | 6·81 |
| 4 O | 32 | 42·68 | 42·80 |
| $C^4NH^5O^4$ | 75 | 100·00 | 100·00 |

Glycolamide has the same composition as glycocol, but is related to it in the same manner as lactamide to alanine (ix, 434; xi, 470). (Dessaignes.) [But lactamide, according to Laurent, is lactamate of ammonia, whereas glycolamide does not contain ammonia (List).]

Glycolamide when treated with potash, does not give off the odour of ammonia till heat is applied. When boiled with potash till ammonia is no longer evolved, it yields glycolic acid. — It is not precipitated by solution of platinum.

## Glycolide.

$C^4H^2O^4 = C^4H^2O^2,O^2$.

DESSAIGNES. *Compt. rend.* 38, 46.

When tartaric acid is heated to 160°, carbonic acid is abundantly evolved together with a body having a peculiar odour; if the temperature be kept at 180°, as long as gas continues to escape, there remains in the retort a slightly coloured mass which has the consistence of turpentine, and solidifies after a few days; it must be pulverised and washed with hot water. White, tasteless, insoluble in cold, very sparingly soluble in hot water. Melts at 180° without loss of weight.

| | | | Dessaignes. |
|---|---|---|---|
| 4 C | 24 | 41·38 | 40·40 |
| 2 H | 2 | 3·45 | 3·75 |
| 4 O | 32 | 55·17 | 55·85 |
| $C^4H^2O^4$ | 58 | 100·00 | 100·00 |

Isomeric with glyoxal.

Glycolide dissolves in potash, producing glycolic acid.

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*Acetic acid.* — Anhydrous acetate of soda treated with protochloride of sulphur yields anhydrous acetic acid :

$$4C^4H^3NaO^4 + 3ClS = 2C^8H^6O^6 + 3NaCl + NaO,SO^3 + 2S.$$

The process cannot however be applied to the preparation of anhydrous acetic acid, inasmuch as the product is contaminated with other bodies, especially sulphur-compounds, which are not easily separated. — Mercurous acetate heated to a temperature between 250° and 300°, yields anhydrous acetic acid mixed with acetone and a body rich in oxygen. (Heintz, *Pogg.* 98, 458.)

*Acetate of Lanthanum.* — Basic acetate of lanthanum, which is precipitated in the form of transparent gelatinous flakes from a solution of oxide or carbonate of lanthanum in excess of acetic acid, by supersaturating with ammonia in the cold after diluting the solution with a large quantity of water,—is coloured deep blue by iodine. The colour is not destroyed by washing with cold water or by drying at ordinary temperatures; but decoloration takes place at 80° (at which temperature the salt still retains water), or by continued boiling of the salt suspended in water; but on adding iodine and a very small quantity of ammonia to the liquid, the colour is restored and blue flakes of the basic salt are precipitated; the colour is also destroyed by addition of acetic, hydrochloric, nitric or sulphuric acid, or of excess of ammonia. — The blueing of basic acetate of lanthanum by iodine takes place only when it is quite free from cerium. It is not exhibited by other basic salts of lanthanum, or by the corresponding salts of alumina, yttria or ceric oxide. (Damour, *Compt. rend.* 43, 976.)

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*Iodide of Ethyl* heated to 100° in sealed tubes with an aqueous or ethereal solution of mercuric chloride, is converted into chloride of ethyl, with simultaneous formation of iodide of silver. — Similarly with the iodides of *methyl* and *amyl*. — When iodide of ethylene is heated for several hours with an aqueous solution of mercuric chloride, it disap-

pears, iodide of mercury is formed, and the liquid, which has a strong acid reaction, yields by distillation, chloride of acetyl, $C^4H^3Cl$:

$$C^4H^4I^2 + 2HgCl = C^4H^3Cl + HCl + 2HgI.$$

(Schlagdenhauffen, *N. J. Pharm.* 29, 247; 30, 38.)

*Bromide of Ethyl* heated with aqueous potash in sealed tubes to 125° for a month, is decomposed, with formation of ether and a small quantity of a gaseous body. At 100°, no complete decomposition takes place, even after heating for 200 hours. (Berthelot, *N. Ann. Chim. Phys.* 43, 282.)

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*Borate of Ethyl.*—H. Rose (*Pogg.* 98, 245), recommends for the preparation of borate of ethyl, $3C^4H^5O,BO^3$, to distil sulphovinate of potash with anhydrous borax between 100° and 120°. If the materials are not quite dry, the ether thus obtained contains water and deposits boracic acid after some time. It does not appear possible to prepare in like manner the ethers of silicic, carbonic, phosphoric, chromic and molybdic acids, or to obtain a compound of oxide of ethyl with alumina.

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## Ethylotrithionic Acid. $C^4H^6S^3O^6$.

J. T. Hobson. *Chem. Soc. Qu. J.* 10, 55.

Obtained in the form of a zinc-salt by the action of sulphurous acid on zinc-ethyl. When perfectly dry sulphurous gas is passed through zinc-ethyl, rapid absorption takes place, and so much heat is evolved that it is necessary to cool the flask during the whole time of the absorption. A crystalline body soon forms, and after some time the flask becomes filled with a quantity of minute crystals, which protect the remaining portion of zinc-ethyl from the action of the gas, so that it is necessary to continue the action for a long time and frequently to break up the crystalline mass. The zinc-salt is purified by recrystallisation, first from alcohol, afterwards from water. It may be converted into a baryta-salt, by treating its boiling solution with caustic baryta, and passing carbonic acid through it till the excess of baryta is precipitated; and from the baryta-salt, the free acid is obtained by precipitating the baryta with dilute sulphuric acid. The zinc-salt distilled with sulphuric acid also yields a distillate of aqueous ethylotrithionic acid; but unless the sulphuric acid used is very dilute, a large portion of the distillate suffers decomposition. After prolonged evaporation over the water-bath it still retains 5 At. water.

The *Ethylotrithionates* are obtained, either by dissolving carbonates in the aqueous acid, or by double decomposition of the baryta-salt with

sulphates. Their general formula is $C^4H^5MS^3O^6$, or $MO,C^4H^5S^3O^5$. The anhydrous acid may be regarded as formed from 3 At. $SO^2$, by the substitution of 1 At. $C^4H^5$ for 1 At. O; thus $C^4H^5S^3O^6 = S^3 \left\{ \begin{matrix} C^4H^5 \\ O^5 \end{matrix} \right.$.

*Ethylotrithionate of Soda.* — $C^4H^5NaS^3O^6$ + Aq. — Obtained by dissolving carbonate of soda in the aqueous acid, evaporating to dryness and extracting with alcohol. The alcoholic solution evaporated in vacuo over sulphuric acid, yields the salt in colourless needle-shaped crystals, very small and not well defined. The crystals dried in vacuo gave by analysis 15·21 p. c. sodium and 30·05 sulphur (by calculation 14·65 Na and 30·57 S).

*Ethylotrithionate of Baryta.* — *Preparation* (p. 513). — Crystallises on cooling from its concentrated aqueous solution, in the form of a colourless pellicle which floats on the surface. The salt, after drying over sulphuric acid in vacuo, gives off 1 At. water at 100°; it sustains a heat of 170° without decomposition.

| | *At* 100°. | | Hobson. | | *Dried over oil of vitriol.* | | Hobson. |
|---|---|---|---|---|---|---|---|
| 4 C | 24·0 | 12·39 | 12·08 | 4 C | 24·0 | 11·84 | 12·11 |
| 5 H | 5·0 | 2·58 | 2·43 | 6 H | 6·0 | 2·96 | 3·03 |
| Ba | 68·6 | 35·43 | 34·41 | Ba | 68·6 | 33·86 | 33·33 |
| 3 S | 48·0 | 24·79 | 24·22 | 3 S | 48·0 | 23·68 | 23·41 |
| 6 O | 48·0 | 24·81 | 26·86 | 7 O | 56·0 | 27·66 | 28·12 |
| $C^4H^5BaS^3O^6$ | 193·6 | 100·00 | 100·00 | + Aq | 202·6 | 100·00 | 100·00 |

*a* was prepared by decomposing the zinc-salt with baryta-water; *b* by saturating the aqueous acid with carbonate of baryta.

*Ethylotrithionate of Zinc.* — *a. Basic.* — The crude salt obtained by the action of sulphurous acid on zinc-ethyl. The excess of oxide of zinc arises from the action of water on the undecomposed zinc-ethyl.

| | | | Hobson. |
|---|---|---|---|
| 8 C | 48·0 | 12·55 | 12·43 |
| 13 H | 13·0 | 3·39 | 3·61 |
| 3 Zn | 97·5 | 25·49 | 25·25 |
| 6 S | 96·0 | 25·09 | 24·80 |
| 16 O | 128·0 | 33·48 | 33·91 |
| $ZnO,2C^4H^5ZnS^3O^6 + 3HO$ | 382·5 | 100·00 | 100·00 |

*b. Normal.* — Obtained by crystallising the basic salt just described, first from alcohol and then from water. Minute, colourless, acicular crystals, having a peculiar odour and a somewhat bitter taste. Dissolves sparingly in water, either hot or cold, and also in ether; nearly insoluble in cold alcohol, but moderate solubly in boiling alcohol. On evaporating the aqueous solution, the salt crystallises out as a pellicle which floats on the surface. It contains 1 At. water of crystallisation, which it does not give off at 100°.

| | | | | Hobson. |
|---|---|---|---|---|
| 4 C | 24·0 | 14·41 | | 14·48 |
| 6 H | 6·0 | 3·60 | | 3·69 |
| Zn | 32·5 | 19·52 | | 19·57 |
| 3 S | 48·0 | 28·82 | | 28·69 |
| 7 O | 56·0 | 33·65 | | 33·57 |
| $C^4H^5ZnS^3O^6 + HO$ | 166·0 | 100·00 | | 100·00 |

*Ethylotrithionate of Copper.* — Obtained either by double decomposition of the baryta-salt, or by dissolving carbonate of copper in the free acid. Crystallises, both from the aqueous and from the alcoholic solution, in greenish blue deliquescent needles.

| *Dried at* 100°. | | | | Hobson. |
|---|---|---|---|---|
| 4 C | 24·0 | 15·33 | | 15·18 |
| 5 H | 5·0 | 3·19 | | 3·29 |
| Cu | 31·6 | 20·18 | | 20·18 |
| 3 S | 48·0 | 30·65 | | 30·20 |
| 6 O | 48·0 | 30·65 | | 31·15 |
| $C^4H^5CuS^3O^6$ | 156·6 | 100·00 | | 100·00 |

*Ethyltrithionate of Silver.* — Prepared by dissolving carbonate of silver in the free acid. White crystalline body, very soluble in water and highly deliquescent. It is not decomposed by exposure to light or by a temperature of 100°, but is entirely decomposed at a temperature a little above.

| *Dried over oil of vitriol in vacuo.* | | | | Hobson (*mean*). |
|---|---|---|---|---|
| 4 C | 24 | 10·30 | | 10·24 |
| 5 H | 5 | 2·15 | | 2·23 |
| Ag | 108 | 46·35 | | 46·18 |
| 3 S | 48 | 20·60 | | 20·49 |
| 6 O | 48 | 20·60 | | 20·86 |
| $C^4H^5ZnS^3O^6$ | 233 | 100·00 | | 100·00 |

*Ethylotrithionate of Ethyl.* — Prepared by distilling the crystallised baryta-salt with sulphovinate of potash in an oil-bath, washing the distillate with water, drying it with chloride of calcium, and redistilling. — Yellow oily liquid, slightly heavier than water and having a disagreeable odour. It is insoluble in water, but mixes in all proportions with alcohol.

| | | | | Hobson. |
|---|---|---|---|---|
| 8 C | 48 | 31·17 | | 30·93 |
| 10 H | 10 | 6·49 | | 6·60 |
| 3 S | 48 | 31·17 | | 31·05 |
| 6 O | 48 | 31·17 | | 31·42 |
| $C^4H^5(C^4H^5)S^3O^6$ | 154 | 100·00 | | 100·00 |

Methylobithionic acid and ethylotrithionic acid (anhydrous) are the first and second terms of a series whose general formula is $S^n\left\{\begin{matrix}C^{2n-2}H^{2n-1}\\ O^{2n-1}\end{matrix}\right.$ the $n$'th term being formed by replacing 1 At. oxygen in $n$-atoms of anhydrous sulphurous acid by 1 At. of the $(n-1)$th term of the series of alcohol-radicals. The sixth term would be amylhexathionic acid $S^6\left\{\begin{matrix}C^{10}H^{11}.\\ O^{11}.\end{matrix}\right.$

## Bisulphetholic Acid.

$C^4H^6S^4O^{12} = C^4H^6,4SO^3$.

BUCKTON & HOFMANN. *Ann. Pharm.* 100, 145; *Chem. Soc. Qu. J.* 9, 249.

*Bisulphetholic acid.*

Obtained by the action of fuming sulphuric acid on propionitrile (cyanide of ethyl), or propionamide. The latter is preferable on account of the greater facility of preparing it. The mode of preparation is similar to that described for bisulphometholic acid (p. 484). The propionamide must be as dry as possible, otherwise the only products obtained are propionic acid and sulphate of ammonia. To ensure this condition, it must be heated in a retort, and only that portion collected which distils above 210°. The proportions required are 1 At. propionamide $C^6NH^7O^2$ to 6 At. $SO^4H$; but as the fuming sulphuric acid of commerce is not of constant composition, its strength must be determined by a special experiment, because too large quantity of acid carbonises the mixture completely, and if too little is used, the chief products are sulphopropionic and propionic acids. The heat must be so regulated as to produce a continuous evolution of carbonic acid. — The residue in the retort is dissolved in water when cold, and treated, first with carbonate of baryta and then with carbonate of ammonia, as in the preparation of bisulphometholic acid. The filtered liquid yields by evaporation a mixture of bisulphetholate and sulphopropionate of ammonia, the latter of which is quite uncrystallisable and may be removed by washing with weak spirit. Bisulphetholate of ammonia then remains on the filter and may be purified by two or three crystallisations from hot water.

The *free acid* is obtained by decomposing the lead-salt with sulphuretted hydrogen. By concentration it forms a thick syrup which ultimately sodifies in a crystalline mass. It is decomposed by heat, with deposition of charcoal and emission of white fumes.

*Bisulphetholate of Ammonia.*— Crystallises from the aqueous solution in colourless regular cubes or square prisms. It is insoluble in alcohol and in ether. Resembles the bisulphometholate, but is more soluble in water, and leaves a carbonaceous residue when strongly heated.

*Bisulphetholate of Baryta.* — $C^4H^4Ba^2S^4O^{12} + 2Aq.$ — Obtained by heating a solution of the ammonia-salt with hydrate of baryta, till the ammonia is completely expelled, and precipitating the excess of baryta by a stream of carbonic acid. — Crystallises in regular six-sided plates, generally radiating from centres. After drying at 100°, it gives off 5·99 p. c. water (2 At.; by calculation 5·24 p. c.) at 220°; the excess perhaps arises from partial decomposition. When strongly heated in close vessels, it blackens, gives off empyreumatic vapours, and leaves a black residue, which burns with a sulphur-flame. It is very soluble in water but insoluble in strong nitric acid, which does not decompose it; from solution in the dilute acid, it crystallises without apparent change.

| | *At* 170°. | | | Buckton & Hofmann. |
|---|---|---|---|---|
| 4 C | 24 | | 7·38 | |
| 4 H | 4 | | 1·23 | |
| 2 Ba | 137 | | 42·15 | 42·36 |
| 4 S | 64 | | 19·69 | 19·68 |
| 12 O | 96 | | 29·55 | |
| $C^4H^4Ba^2S^4O^{12}$ | 325 | | 100·00 | |

When the salt is fused with chlorate of potash and carbonate of soda, and the fused mass is treated with water, the filtered solution is found to contain sulphates, showing that the salt contains more sulphur than is required to saturate the barium. This reaction distinguishes the bisulphetholates from the sulphopropionates.

*Bisulphetholate of Lead.* — Easily soluble in water. The solution when evaporated over oil of vitriol, yields thin prisms and four-sided laminæ; when quickly evaporated, it thickens to a viscid gummy mass.

*Bisulphetholate of Silver.* — Obtained like the bisulphometholate. Crystalline. In the dry state, it bears a tolerably high temperature without decomposition, but the solution blackens when boiled.

# ADDITIONS TO VOL. IX.

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*Mesitylo-sulphuric acid.* — Kane, by acting upon acetone with strong sulphuric acid, obtained two acids, viz., mesitylo-sulphuric and permesitylo-sulphuric acid, the lime-salt of the first containing $C^6H^5CaO^2,SO^3$, and of the second $C^6H^6O^2.2(CaO,SO^3)$. According to Hlasiwetz (*Wien. Akad. Ber.* 21, 225), acetone treated with monohydrated sulphuric acid or fuming sulphuric acid in various proportions—the mixture being cooled to moderate the action—always yields an acid having nearly the composition of the former of these acids. The mixture, after the action had ceased, was diluted with water, saturated with carbonate of lime, strained, filtered, and evaporated at a gentle heat, the sulphate of lime being removed as it separated; and the resulting lime-salt, which formed small crystals or a gummy mass, was purified by solution in hot alcohol and precipitation with ether. It was thereby obtained as a gelatinous pulp, which dried up to a white or slightly yellow powder, having nearly the composition of the lime-salt of the acid $C^6H^6O^2,S^2O^4$.

| | *Dried at* 100°. | | Hlasiwetz. |
|---|---|---|---|
| CaO | 28 | 19·8 | 20·3 to 22·7 |
| 6 C | 36 | 25·5 | 27·8 „ 28·7 |
| 5 H | 5 | 3·6 | 4·0 „ 4·1 |
| 2 S | 32 | 22·7 | |
| 5 O | 40 | 28·4 | |
| $C^6H^5CaO^2,S^2O^4$ | 141 | 100·0 | |

Hlasiwetz regards the salt analysed as still impure.

By decomposing the lime-salt with carbonate of ammonia, evaporating the filtrate, exhausting the residue with strong alcohol, and leaving the solution to evaporate, a buttery deliquescent mass was obtained, which, when heated with potash, gave off ammonia and yielded a distillate of oxide of mesityl.

A *copper-salt* $C^6H^5CuO^2,S^2O^4+2Aq$, was obtained by exactly decomposing the solution of the lime-salt with sulphate of copper. It separates from boiling alcohol in greenish crystalline needles.

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## Acetal. $C^{12}H^{14}O^4 = \left.\begin{matrix} C^4H^4 \\ (C^4H^5)^2 \end{matrix}\right\} O^4.$

WURTZ. *N. Ann. Chim. Phys.* 48, 370.

*Ethylate of Ethylene.*

Wurtz prepares this compound by distilling 2 pts. of alcohol with 3 pts. of peroxide of manganese, 3 pts. of oil of vitriol and 2 pts. of water (the proportions recommended by Liebig for the preparation of aldehyde). As soon as the effervescence which at first takes place has subsided, 3 pts. of the liquid are distilled off; the distillate is rectified; and the portion A which distils below 80° (the thermometer being immersed in the vapour) is separated from the portion B which passes over between 80° and 95°. The former portion is placed in contact with pulverised chloride of calcium and rectified. The portion which then distils below 60° consists chiefly of liquid containing aldehyde, and above 60° a distillate is obtained from which, on addition of concentrated of chloride of calcium, an ethereal layer separates. The portion B of the former distillate (boiling between 80° and 95°) is likewise rectified; and from the portion which first passes over, an ethereal layer is also separated by addition of chloride of calcium. The ethereal liquids thus separated, containing aldehyde, acetic ether, &c., and acetal, are united, and shaken up with caustic potash, whereby the aldehyde is resinised and the greater part of the compound ethers decomposed. The brown liquid which then floats upon the potash-solution, is separated and distilled; the distillate again mixed with chloride of calcium; the liquid thereby separated is heated with twice its volume of potash-ley to 100° in a sealed tube for 24 hours; the lighter stratum rectified; the distillate again shaken up with chloride of calcium; and the separated layer digested with pulverised chloride of calcium and rectified alone. Pure acetal then passes over between 100° and 105°.

| | | | Wurtz. |
|---|---|---|---|
| 12 C | 72 | 61·02 | 60·61 |
| 14 H | 14 | 11·86 | 11·84 |
| 4 O | 32 | 27·12 | 27·55 |
| $C^{12}H^{14}O^4$ | 118 | 100·00 | 100·00 |

[Stas (ix, 40) regarded acetal as a compound of 1 At. aldehyde with 2 At. ether $C^4H^4O^2 + 2C^4H^5O]^2$. Wurtz regards it as glycol or hydrate of ethylene $\left.\begin{matrix} C^4H^4 \\ H^2 \end{matrix}\right\} O^4$ having the two basic atoms of hydrogen replaced by 2 At. ethyl. This view is confirmed by the formation of the compounds described below.

Acetal is dissolved by strong hydrochloric acid. The liquid if left to itself blackens at the end of two days, and then holds in solution a considerable quantity of chloride of ethyl. — Pentachloride of phosphorus acts upon it energetically, giving off a considerable quantity of chloride

of ethyl. — Mixed with several times its weight of glacial acetic acid and heated in a sealed tube placed in the oil-bath, it yields acetic ether, each atom of acetal yielding more than 1 At. acetic ether.

*Methylate of Ethylene*, $C^{10}H^{10}O^4 = \left.\begin{matrix} C^4H^4 \\ (C^2H^3)^2 \end{matrix}\right\} O^4$. — Obtained, together with the following compound, by mixing in a capacious retort, 110 pts. of alcohol and 90 pts. of wood-spirit with 300 pts. of oil of vitriol, 300 pts. of water and 200 pts. of peroxide of manganese. As soon as the first effervescence has subsided, the mixture is distilled till a quantity of liquid has passed over equal to that of the mixture of alcohol and wood-spirit used, and this product is rectified, the portions which go over above and below 68° being collected separately, and the distillation stopped at 85°. These two portions are rectified, as in the preparation of acetal, then shaken up with chloride of calcium, and the liquid treated several times with caustic potash. An ethereal product is thus obtained having a peculiar odour and containing acetal and the intermediate compounds, together with a trace of methylal. On subjecting this mixture to fractional distillation, a considerable portion of liquid passes over between 60° and 70°, and another between 80° and 90°. These when purified by further fractional distillation, ultimately yield a product boiling at about 65°, which is methylate of ethylene, and another boiling at about 85°.

Methylate of ethylene is a colourless mobile liquid having an ethereal odour, like the methyl-compounds in general. Sp. gr. 0·8555 at 0°. It burns with a bright white flame bordered with blue. Dissolves in a large quantity of water.

| | | | Wurtz. |
|---|---|---|---|
| 8 C | 48 | 53·33 | 53·69 |
| 10 H | 10 | 11·11 | 11·31 |
| 4 O | 32 | 35·56 | 35·00 |
| $C^8H^{10}O^4$ | 90 | 100·00 | 100·00 |

Acetal in which the ethyl is entirely replaced by methyl, or glycol, in which the 2 At. basic hydrogen are thus replaced.

*Methylethylate of Ethylene* or *Methylacetal*, $C^{10}H^{12}O^4 = \left.\begin{matrix} C^4H^4 \\ C^2H^3,C^4H^5 \end{matrix}\right\} O^4$. — This is the product which boils at about 85°. It is a very mobile liquid having a penetrating ethereal odour, like that of acetal itself. Sp. gr. 0·8535. Vapour-density, 3·475. It dissolves in about 15 times its bulk of water and in all proportions of alcohol. It is precipitated from its alcoholic solution by water and more especially by aqueous chloride of calcium; if however the alcohol is in excess, water does not separate any thing from the solution.

| | | | Wurtz. | | Vol. | Density. |
|---|---|---|---|---|---|---|
| 10 C | 60 | 57·69 | 57·77 | C-vapour | 10 | 4·1600 |
| 12 H | 12 | 11·53 | 11·64 | H-gas | 12 | 0·8316 |
| 4 O | 32 | 30·78 | 30·59 | O-gas | 2 | 2·2186 |
| $C^{10}H^{12}O^4$ | 104 | 100·00 | 100·00 | Vapour of $C^{12}H^{10}O^4$ | 2 | 7·2102 |
| | | | | | 1 | 3·6051 |

Acetal in which 1 At. ethyl is replaced by methyl.

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*Triethylamine.*—This compound may be prepared by digesting cyanate of ethyl with pure ethylate of potassium or sodium (absolute alcohol saturated as far as possible with potassium or sodium) for several hours at a moderate heat, and subsequently distilling on a sand-bath. A strongly alkaline liquid is thus obtained, which, when saturated with hydrochloric acid, yields, on evaporation to dryness, a residue from which a considerable quantity of triethylamine is expelled on addition of potash. The reaction, which is expressed by the equation,

$$C^2N(C^4H^5)O^2 + 2C^4H^5KO^2 = N(C^4H^5)^3 + 2KO,CO^2,$$

is precisely analogous to that by which ethylamine is obtained in the action of hydrate of potash on cyanate of ethyl :

$$C^2N(C^4H^5)O^2 + 2HKO^2 = N(C^4H^5,H^2) + 2KO,CO^2.$$

A quantity of the base prepared as above yielded an orange-coloured platinum-salt, which gave by analysis 32·73 and 32·55 p. c. of platinum, the formula requiring 32·12 p. c. The slight excess of platinum is due to admixture of ethylamine, the formation of which arises from a trace of moisture in the ethylate of potassium or the cyanate of ethyl. In fact, if great care be not taken to dry the materials, ethylamine is the principal product formed. (Hofmann, *Chem. Soc. Qu. J.* 10,208.)

## Triethylphosphine.

$C^{12}H^{15}P = (C^4H^5)^3P.$

HOFMANN & CAHOURS. *Phil. Trans.* 1857, 575; *Ann. Pharm.* 104, 110; *Chem. Soc. Qu. J.* 11.

*Formation.* By the action of terchloride of phosphorus on zinc-ethyl.

$$PCl^3 + 3C^4H^5Zn = (C^4H^5)^3P + 3ZnCl.$$

*Preparation.* A tubulated retort *f*, is joined to a receiver *e*, which, in its turn is connected with a wide glass tube *d*, bent at an angle of about 130°, and acting like a second receiver. The angle of this tube is filled with terchloride of phosphorus, and the tube is connected with a large cylinder *c*, which is supplied by a suitable apparatus *a*, *b*, with dry carbonic acid. As soon as the carbonic acid has expelled the air from the reservoir, tube, receiver, and retort, an exit-tube from the reservoir, up to that time closed by a caoutchouc cap, is opened to let out the carbonic acid, the evolution of which is maintained during the whole operation. The tubulature of the retort is now connected with the copper digester in which the zinc ethyl has been prepared ; and as soon as the retort has received a charge of the ethereal solution of zinc-ethyl, there is fixed into the same tubulature a little dropping apparatus *g*, consisting of a glass globe, with a tubulature and stopper at the top, and terminating below in a glass tube in which a stopcock is fitted. This apparatus is filled with terchloride of phosphorus, and by appropriately adjusting the

stopcock and opening or closing the stopper of the glass globe, any desired flow of the liquid can be maintained with the greatest nicety. However slowly the action may be accomplished, and however well, moreover,

the retort and receiver may be cooled by water or ice, the action is nevertheless so violent, that all the ether, and with it a large quantity of the zinc-ethyl, passes over into the receiver. By the powerful ebullition which periodically ensues, a portion of the vapour is driven even into the bent tube, and a considerable loss of zinc-ethyl is incurred, unless this tube is filled with terchloride of phosphorus, which greedily absorbs every trace of the former compound. This fluid valve, ascending and descending in the tube, in accordance with the progress of the reaction, regulates the function of the apparatus so perfectly, that the operation, which always takes several hours, continues by itself when once begun. Sometimes the absorption is so violent that the terchloride of phosphorus in the tube is sucked back into the receiver; but even then no loss is to be feared, since the tube is connected with the reservoir filled with carbonic acid. The first drops of terchloride of phosphorus which fall into the solution of zinc-ethyl, hiss like water coming in contact with red-hot iron. The action becomes by-and-by less violent, and as soon as an evolution of heat is no longer perceptible, the operation is terminated. There remain in the retort, in the receiver, in the bent tube, and sometimes even in the carbonic acid reservoir, two liquid layers,—the one a heavy pale straw-coloured thick fluid, the other a transparent colourless mobile fluid floating on the former.

The heavy fluid, a compound of the phosphorus-base with chloride of zinc, nearly solidifies on cooling; but the viscid transparent mass exhibits no trace of crystalline structure. The light fluid is a mixture of ether with an excess of the terchloride of phosphorus; after disconnecting the apparatus, it is poured off from the viscous fluid, and may be used, after distillation, in a second operation. Some ether and terchloride of phosphorus which may still adhere are expelled by gently heating the retort upon a sand-bath.

The phosphorus-base is liberated from its combination with zinc by distillation with potash. To prevent destruction of the retort, and loss of material, this operation is conveniently performed in the following manner. Solid hydrate of potash is placed on the hard resinous cake attached to the bottom of the retort, and a slow current of water allowed to flow in by the dropping apparatus, after the air in the retort has been carefully displaced by hydrogen: the heat evolved during the reaction

is quite sufficient to volatilise the base with the vapour of the water; it may be condensed by an ordinary cooler. The base, which is now floating on the water of the distillate, is removed by means of a separating funnel; it is allowed to stand for a day over hydrate of potash, and finally rectified in a current of dry hydrogen gas.

*Properties.* Transparent, colourless, mobile liquid which strongly refracts light. Sp. gr. 0·812 at 15°. Boils at 127·5 under a barometric pressure of 0·744 mm. Its odour is penetrating, almost benumbing but still not disagreeable, and in a diluted state, resembles that of the hyacinth. The intolerable odour which usually attends the preparation of this and the other phosphorus-bases, arises from the formation of other products. Long-continued working with this substance produces head-ache and sleeplessness. When recently prepared, it is without action on vegetable colours, but if exposed to the air for a few seconds, it shows a constantly increasing acid reaction.

| | | | | Hofmann & Cahours. |
|---|---|---|---|---|
| 12 C | 72 | | 61·01 | 60·00 |
| 15 H | 15 | | 12·71 | 12·68 |
| P | 31 | | 26·28 | |
| $(C^4H^5)^3P$ | 118 | | 100·00 | |

The analysis exhibits a small loss of carbon, arising from oxidation in the previous manipulations.

*Decompositions.* 1. When brought in contact with *oxygen* gas, it emits vapours, and frequently takes fire, emitting dense white fumes of phosphoric acid. If a strip of paper moistened with triethylphosphine be introduced into a test-tube containing oxygen and immersed in hot water, the vapour of the phosphorus-base forms with the oxygen an explosive mixture which detonates violently after a few moments. — 2. When triethylphosphine is poured into a flask containing *chlorine*, every drop takes fire, with formation of hydrochloric acid and pentachloride of phosphorus, and separation of carbon. If however the action be moderated, crystalline compounds are produced. — 3. In *cyanogen*-gas, triethylphosphine is converted into a resinous mass.

*Combinations.* Triethylphosphine has a powerful affinity for oxygen and sulphur, less for selenium. Its combinations with these bodies contain 2 At. of the electro-negative element to 1 At. triethylphosphine.

It is perfectly insoluble in water.

*Oxide of Triethylphosphine.* — $(C^4H^5)^3PO^2$. — Obtained: 1. By the direct oxidation of the phosphorus-base. This substance has so strong an attraction for oxygen, that it cannot be distilled without oxidation except in an atmosphere of hydrogen or carbonic acid. In contact with pure oxygen, it suffers decomposition (*vid. sup.*) When the larger quantity of the base has distilled over, the boiling point suddenly rises, and the neck of the retort becomes covered with a beautiful network of crystals of the oxide. — 2. By gently heating triethylphosphine with oxide of mercury or oxide of silver. Considerable evolution of heat then takes place, the metal is reduced, and oxide of triethylphosphine separates in oily drops, or sometimes sublimes in radiated crystals. It also separates in oily drops when

triethylphosphine is boiled with strong nitric acid, and potash added to the highly concentrated liquid. — 3. By the action of heat on the hydrated oxide of tetrethylphosphonium :

$$(C^4H^5)^4PO,HO = (C^4H^5)^3PO^2 + \underbrace{C^4H^6}_{\text{hydride of ethyl.}}.$$

On subjecting this body to distillation, water passes over at first; but when the liquid has attained a certain degree of concentration, gaseous hydride of ethyl is given off. On continuing the heat, the evolution of gas ceases; and at 200°, a viscid nearly inodorous liquid distils over, the temperature then slowly rising, till, at about 240°, the boiling point becomes stationary and the distillate then generally solidifies in a crystalline mass in the neck of the retort.

Oxide of triethylphosphine forms colourless crystals, which are so deliquescent that a crystal exposed to the air liquefies entirely in a few seconds. In perfectly dry air, however they are permanent. On fusing the crystalline mass by the heat of a spirit-lamp and collecting the liquid in a receiver, it often solidifies instantaneously on cooling, but sometimes remains liquid for months. It may be obtained perfectly dry and solid by distillation with anhydrous phosphoric acid, but suffers partial decomposition at the same time. — It is decomposed by potassium, with separation of triethylphosphine. — It dissolves in all proportions in water and in alcohol, but is less soluble in ether. The aqueous solution is precipitated by potash, the oxide then separating in colourless oily drops, which remain liquid even after much concentration, and rapidly dissolve on diluting the potash-solution with a comparatively small quantity of water. — The oxide dissolves readily in acids.

*Sulphide.* — $(C^4H^5)^3PS^2$. — Obtained : 1. By the direct combination of triethylphosphine with sulphur. Flowers of sulphur are gradually introduced into an ethereal solution of triethylphosphine till a portion remains undissolved, the liquid effervescing on each addition. The ether is then volatilised, and the residuary mixture of the sulphide and free sulphur treated with boiling water, which dissolves the sulphide and on cooling deposits it in crystals of perfect purity. — 2. By distilling triethylphosphine with cinnabar, which is then reduced to subsulphide or to metallic mercury. — The compound is not formed by treating the oxide with sulphuretted hydrogen or sulphide of ammonium.

By slowly cooling the aqueous solution, the compound is obtained in beautiful needle-shaped crystals often five or six inches long. It melts at 94°, and resolidifies at 88°. When heated beyond 100°, it is volatilised and diffuses a white vapour having a disagreeable sulphur-odour, which is but slightly perceptible at common temperatures. When heated with a quantity of water not sufficient for its solution, it rises to the surface in the form of a transparent oil, which is copiously volatilised with the aqueous vapour.

| | | | Hofmann & Cahours |
|---|---|---|---|
| $(C^4H^5)^3P$ | 118 | 78·67 | |
| 2 S | 32 | 21·33 | 21·74 |
| $(C^4H^5)^3PS^2$ | 150 | 100·00 | |

The sulphide is instantaneously decomposed by potassium, with separation of triethylphosphine.

It is much more soluble in hot than in cold water, only a small quantity remaining dissolved at ordinary temperatures. It is still less soluble in alkaline liquids. On adding an alkali to the cold aqueous solution, the mixture becomes turbid and soon deposits small crystals. On adding potash to the boiling saturated aqueous solution, the sulphide instantly separates in oily drops, which, as the liquid cools, rapidly solidify into spherical aggregates of crystals. — It dissolves even more readily in alcohol and ether, and in bisulphide of carbon almost without limit; from this solvent it does not crystallise perfectly.

The aqueous solution is without action on vegetable colours; the compound nevertheless appears to possess faintly basic properties. It dissolves more readily in hydrochloric acid, especially when concentrated, than in water, and the solution furnishes with bichloride of platinum a yellow precipitate, which rapidly cakes into a resinous mass, giving indications of decomposition by the separation of bisulphide of platinum. The sulphur-compound also dissolves in dilute sulphuric and nitric acids; concentrated nitric acid decomposes it; the fuming acid gives rise to a sort of detonation. The aqueous solution is not affected by acetate of lead, nitrate of silver, or protoxide of mercury, even at the boiling temperature; the alcoholic solution, on the other hand, is instantaneously decomposed, with separation of sulphide of lead, silver, or mercury. The liquid filtered off from the precipitate now contains the oxide of triethylphosphine, either free or in the form of acetate or nitrate, and easily separable by the addition of an alkali.

*Selenide.* — $(C^4H^5)^3PSe^2$. — Prepared, like the sulphide, by the direct combination of triethylphosphine with selenium; the reaction however is less powerful than with sulphur. — Crystallises from water as easily as the sulphide, but the solution is apt to undergo partial decomposition when exposed to the air. Even the dry crystals are slowly reddened in the air. Melts at 112°, and is easily volatilised with partial decomposition.

| | | | Hofmann & Cahours. |
|---|---|---|---|
| $(C^4H^5)^3P$ | 118 | 59·9 | |
| 2 Se | 79 | 40·1 | 39·45 |
| $(C^4H^5)^3PSe^2$ | 197 | 100·0 | |

*Chloride, Bromide, and Iodide of Triethylphosphine.*—Oxide of triethylphosphine, when treated with hydrochloric, hydrobromic or hydriodic acid, is converted into the corresponding chloride, bromide, or iodide, which closely resemble the oxide in their general properties. They are liquids which gradually solidify in the exsiccator; the crystals fuse at 100° and begin to volatilise, although their boiling-point is very high. The compounds of triethylphosphine with chlorine, bromine, and iodine may also be obtained by the action of these elements in aqueous or alcoholic solutions upon the phosphorus-base itself. Both methods, however, furnish products which are difficult to purify.

Triethylphosphine forms crystalline compounds with hydrochloric, hydrobromic, hydriodic, sulphuric and nitric acids; but they can be obtained in the dry state only by means of the exsiccator.

*Chloroplatinate of Triethylphosphine.* — The solution of the base in hydrochloric acid affords a crystalline platinum-salt, which is insoluble in cold water, in alcohol and in ether, and decomposes at 100°.

| | *Dried over oil of vitriol.* | | | Hofmann & Cahours. |
|---|---|---|---|---|
| 12 C | 72·0 | .... | 22·21 | |
| 16 H | 16·0 | .... | 4·94 | |
| P | 31·0 | .... | 9·56 | |
| 3 Cl | 106·5 | .... | 32·85 | ..... 32·96 |
| Pt | 98·7 | .... | 30·44 | ..... 30·59 |
| $(C^4H^5)^3P,HCl,PtCl^2$ | 324·2 | .... | 100·00 | |

The platinum in this and the corresponding salts of the other phosphorus-bases cannot be determined in the ordinary way by simple ignition, because a considerable quantity of it is carried off with the phosphorus-vapour, however slowly and carefully the process may be carried out; but by heating with a considerable excess of carbonate of soda in a porcelain crucible on a sand-bath, the temperature of which is gradually raised, the determination succeeds without difficulty. After removal of the portion soluble in water, the platinum-residue, which is always contaminated with silicic acid, is dissolved in nitrohydrochloric acid, the solution evaporated to dryness, and the residue again dissolved in acid: the careful evaporation of this solution furnishes a perfectly accurate result. This method, though somewhat tedious, has the advantage of affording a simultaneous determination of the chlorine.

## Tetrethylphosphonium.

$C^{16}H^{20}P = (C^4H^5)^4P.$

HOFMANN & CAHOURS. *Phil. Trans.* 1857, 583.

Obtained as an iodide by the action of iodide of ethyl on triethylphosphine:

$$C^{14}H^{15}P + C^4H^5I = C^{16}H^{20}P,I.$$

Not known in the separate state. It may be regarded as ammonium in which the nitrogen is replaced by phosphorus and the 4 At. H by 4 At. $C^6H^5$.

*Hydrated Oxide.* — $(C^4H^5)^4PO,HO$. — Obtained by the action of oxide of silver on the iodide. A strongly alkaline solution is formed which retains a small quantity of silver in solution.

This liquid, which is almost without odour, and has a bitter and phosphoric taste, dries up when placed over sulphuric acid, into a crystalline extremely deliquescent mass, the silver separating at the same time in the form of a black powder, or as a brilliant metallic mirror. The mass, when redissolved in water, furnishes a colourless liquid free from silver, but generally containing carbonic acid. It attracts both water and carbonic acid with avidity.

In its deportment with other substances, this oxide resembles the oxide of tetrethylium (ix, 66), its solution exhibiting all the reactions of a solution of potash; the precipitates, such as alumina and protoxide of zinc, dissolve, however, less readily in excess of the phosphorus-compound.

The hydrated oxide is resolved by heat into hydride of ethyl and binoxide of triethylphosphine (p. 524). If however it has been exposed for some time to the air and has absorbed carbonic acid, a different decomposition takes place, the carbonate of tetrethylphosphonium being resolved into triethylphosphine and carbonate of ethyl, which passes over in the form of an inflammable aromatic liquid, without any evolution of permanent gas:

$$(C^4H^5)^4PO,CO^2 = (C^4H^5)^3P + C^4H^5O,CO^2.$$

*Iodide.* — $(C^4H^5)^4PI$. — On mixing triethylphosphine with iodide of ethyl, a violent action ensues after a few moments, the liquid effervescing with almost explosive violence and then solidifying in a white crystalline mass. If an ethereal solution of triethylphosphine is used, the crystals form more slowly. The iodide is very soluble in water, less soluble in alcohol, insoluble in ether. The aqueous solution crystallises on addition of potash-solution, in which this compound, like the iodides of tetramethylium and tetrethylium (vii, 320; ix, 66) is but slightly soluble. From the alcoholic solution it is deposited, on addition of ether, as a crystalline powder. If ether be added to a cold alcoholic solution, as long as the precipitate first formed is dissolved by boiling, well-formed crystals of the iodide are deposited on cooling.

| | | | Hofmann & Cahours. |
|---|---|---|---|
| $(C^4H^5)^4P$ | 147 | 53·65 | |
| I | 127 | 46·35 | 46·25 |
| $(C^4H^5)^4PI$ | 274 | 100·00 | |

Tetrethylphosphonium produces crystallisable salts with hydrochloric, nitric, and sulphuric acids. All these compounds exhibit the deliquescent character of the oxide. Like the latter, they are also soluble in alcohol; in ether they are for the most part insoluble. The hydrochloric solution forms sparingly soluble precipitates with bichloride of platinum and terchloride of gold.

*Chloroplatinate.* — The pale orange-yellow precipitate which falls on addition of bichloride of platinum to a moderately dilute solution of the chloride, dissolves with difficulty, but without decomposition, in boiling water; it is insoluble in alcohol and in ether.

| | *At* 100°. | | Hofmann & Cahours. |
|---|---|---|---|
| $C^{16}H^{20}P$ | 147·0 | 41·75 | |
| 3 Cl | 106·5 | 30·23 | 30·13 |
| Pt | 98·7 | 28·02 | 27·82 |
| $(C^4H^5)^4PCl,PtCl^2$ | 352·2 | 100·00 | |

*Chloroaurate.* — The crystalline precipitate obtained on mixing hydrochlorate of tetrethylphosphonium with terchloride of gold, separates from boiling water in brilliant yellow needles.

| | *At* 100°. | | Hofmann & Cahours. |
|---|---|---|---|
| $C^{16}H^{20}P$ | 147 | 30·25 | |
| 4 Cl | 142 | 29·22 | |
| Au | 197 | 40·53 | 40·22 |
| $(C^4H^5)^4PCl,AuCl^3$ | 436 | 100·00 | |

## Methyltriethylphosphonium.

$C^{14}H^{18}P = (C^2H^3)(C^4H^5)^3P.$

HOFMANN & CAHOURS. *Phil. Trans.* 1857, 590.

*Iodide.* $(C^2H^3)(C^4H^5)^3PI$. — Obtained by the action of iodide of methyl on triethylphosphine. The action is still more violent than in the case of iodide of ethyl (p. 527), and unless ether is added, a portion of the product is very apt to be lost. The compound separates in crystals, which, when dried at 100°, contain 48·77 p. c. iodine, the formula requiring 48·85 p. c.

The solution of the iodide treated with oxide of silver, yields a strongly alkaline solution of the *hydrated oxide.*

*Chloroplatinate.* — The alkaline solution saturated with hydrochloric acid and mixed with bichloride of platinum, yields a beautiful orange-yellow platinum salt, crystallising in well defined cubes truncated by the planes of the octohedron. It is insoluble in alcohol and ether, and may be recrystallised from boiling water without decomposition.

| | | | Hofmann & Cahours. |
|---|---|---|---|
| $C^{14}H^{18}P$ | 133·0 | 39·20 | |
| 3 Cl | 106·5 | 31·49 | 31·72 |
| Pt | 98·7 | 29·31 | 29·55 |
| $(C^2H^3)(C^4H^5)^3PCl,PtCl^2$ | 338·2 | 100·00 | |

## Trimethylethylphosphonium.

$C^{10}H^{14}P = (C^2H^3)^3(C^4H^5)P.$

HOFMANN & CAHOURS. *Phil. Trans.* 1857, 595.

*Iodide.* $(C^2H^3)^3(C^4H^5)P$. — Obtained by the action of iodide of ethyl on an ethereal solution of trimethylphosphine (p. 491). Crystallises readily from boiling water. It yielded by analysis 53·67 p. c. iodine. (Calculation, 54·76 p. c.)

*Chloroplatinate.* — Yellow salt insoluble in alcohol and ether, but rather soluble in water, and crystallises from the boiling solution in magnificent octohedrons.

| | | | Hofmann & Cahours. |
|---|---|---|---|
| $C^{10}H^{14}P$ | 105·0 | 33·86 | |
| 3 Cl | 106·5 | 34·33 | 33·95 |
| Pt | 98·7 | 31·81 | 31·72 |
| $(C^2H^3)^3(C^4H^5)PCl,PtCl^2$ | 310·2 | 100·00 | 100·00 |

## Trimethylamylphosphonium.

$C^{16}H^{20}P = (C^2H^3)^3(C^{10}H^{11})P.$

HOFMANN & CAHOURS. *Phil. Trans.* 1857, 596.

*Iodide.* $C^{16}H^{20}PI$. — Deposited slowly from an ethereal mixture of iodide of amyl and trimethylphosphine. Extremely soluble in water, so that if the ethereal solution of iodide of amyl contains only a trace of water, the salt separates in the form of a syrup which only gradually solidifies. From absolute alcohol it crystallises, though with difficulty, in needles. It gave by analysis 46·22 p. c. iodine, the formula requiring 46·35 p. c.

*Chloroplatinate.* — The oxide liberated from the iodide by means of oxide of silver, yields, with hydrochloric acid and bichloride of platinum, a very soluble platinum-salt, which crystallises from boiling water in splendid needles aggregated in spherules.

| | | | Hofmann & Cahours. |
|---|---|---|---|
| $C^{16}H^{20}P$ | 147·0 | 41·74 | |
| 3 Cl | 106·5 | 30·24 | 30·24 |
| Pt | 98·7 | 28·02 | 27·91 |
| $(C^2H^3)^3(C^{10}H^{11})PCl,PtCl^2$ | 352·2 | 100·00 | |

## Triethylamylphosphonium.

$C^{22}H^{26}P = (C^4H^5)^3(C^{10}H^{11})P.$

HOFMANN & CAHOURS. *Phil. Trans.* 1857, 591.

*Iodide.* $C^{22}H^{26}PI$. — Iodide of amyl acts but slowly on triethylphosphine. An ethereal mixture of the two substances deposits in a few days beautiful crystals, which may be purified by solution in alcohol and precipitation by ether. They contain 40·45 p. c. iodine (by calculation 40·20 p. c.).

*Hydrated oxide.* — Obtained by treating the iodide with oxide of silver. Resembles the oxide of tetrethylphosphonium. When heated, it gives off a small quantity of inflammable gas, probably hydride of ethyl, a liquid being also formed which boils at about 280°, and appears to be the binoxide of biethylamylphosphine:

$$(C^4H^5)^3(C^{10}H^{11})PO,HO = (C^4H^5)^2(C^{10}H^{11})O^2 + C^4H^5,H.$$

*Chloroplatinate.* — The solution of the hydrated oxide in hydrochloric acid deposits, on addition of bichloride of platinum, a beautiful platinum-salt, which crystallises in prisms with flat terminal planes. It is insoluble in alcohol and ether but rather soluble in water.

| | | | Hofmann & Cahours. |
|---|---|---|---|
| $C^{22}H^{26}P$ | 189·0 | 47·94 | |
| 3 Cl | 106·5 | 27·02 | 27·42 |
| Pt | 98·7 | 25·04 | 25·18 |
| $(C^4H^5)^3(C^{10}H^{11})PCl,PtCl^2$ | 394·2 | 100·00 | |

## Cadmium-ethyl.

J. A. Wanklyn. *Chem. Soc. Qu. J.* 9, 193.

Obtained by the action of cadmium on iodide of ethyl. Thin cadmium foil was enclosed, together with half its weight of iodide of ethyl dissolved in an equal volume of ether, in a sealed tube, and heated, as in Frankland's preparation of zinc-ethyl (x, 530), at first to 130° for an hour and afterwards to 100° for 30 or 40 hours. On opening the vessel, a large quantity of gas escaped, and when the contents of the tube were distilled in an atmosphere of carbonic acid, ether and excess of iodide of ethyl passed over at first, and between 180° and 220°, a colourless liquid, which gave off white and afterwards brown vapours on exposure to the air, and at length took fire, emitting a brown smoke. It had an odour like that of zincethyl, and was decomposed by water, with effervescence and formation of a white precipitate. It contained 36 8 p. c. of cadmium, whereas the formula $C^4H^5Cd$ requires 66 per cent. This would show that the distillate contained about 56 per cent of cadmium-ethyl, the remainder consisting of ether, iodide of ethyl, and perhaps certain hydrocarbons.

In another experiment, in which cadmium was heated with iodide of ethyl and ether to 125°, for two or three days, the portion which distilled above 170° yielded on rectification between 95° and 165° (no constant boiling point was observed), a liquid which fumed but slightly in the air and did not take fire spontaneously; the residue contained metallic cadmium.

When cadmium, iodide of ethyl and ether were heated together for a considerable time to 100° in a sealed tube, the action began after several hours only, a crystalline powder then separating; when the tube was opened, the contents did not fume, the crystalline powder became hot on exposure to the air, and effervesced with water. It appears probable that, in the action of cadmium on iodide of ethyl, a compound of cadmium-ethyl and iodide of cadmium is formed, and that the greater part of the cadmium-ethyl is decomposed at the temperature required to liberate it from this compound, a small portion only being carried over undecomposed, together with the hydrocarbons resulting from the decomposition. (Wanklyn.)

Sonnenschein (*J. pr. Chem.* 67, 169,) by heating an alloy of cadmium and sodium with iodide of ethyl in a sealed tube, obtained a white crystalline mass, which was insoluble in water, soluble in iodide of ethyl, and had an extremely penetrating unpleasant odour, like that of musk.—The action of cadmium on iodide of ethyl was tried by Schüler in 1853, (*Ann. Pharm.* 87, 34,) but without any definite result.)

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## Iodide of Acetyl. $C^4H^3O^2,I$.

A. CAHOURS. *Compt. rend.* 44, 1252; *Ann. Pharm.* 104, 109.
F. GUTHRIE. *Ann. Pharm.* 103, 335.

*Iodide of Othyl.*

*Formation* By the action of iodide of phosphorus on anhydrous acetic acid (Guthrie), or anhydrous acetate of potash. (Cahours.)

*Preparation.* 1. Anhydrous acetic acid (1 At.) is poured upon more than 1 At. of dry phosphorus in a long-necked flask, and rather more than 1 At. dry iodine gradually added by small portions. The flask is then heated till the action is complete, and the liquid still containing free iodine, is poured into a retort containing a few pieces of dry phosphorus, and having its neck turned upwards and connected with a condensing apparatus. After the liquid has been boiled in this manner for some minutes, the neck of the retort is turned downwards and the liquid distilled off. The boiling point remains almost constant at 108°, but towards the end, when there is but little liquid remaining, it rises to 120°. The distillate is well shaken with mercury till it becomes transparent, then quickly poured off and rectified, the portion which distils at 108° being collected apart. However carefully the distillation may be conducted, part of the iodide of acetyl is decomposed, hydriodic acid escaping, and a solid substance containing iodine, probably a substitution-product, remaining. 3¾ oz. of anhydrous acetic acid treated as above with 9½ oz. of iodine and about 1 oz. of phosphorus, yielded about 5 oz. of iodide of acetyl. (Guthrie.)

*Properties.* Transparent colourless liquid. (Cahours.) When first prepared it has a brownish colour, which, according to Guthrie, is peculiar to it, and cannot be removed by agitation with mercury; Cahours however states that the colour is completely removed by agitation with mercury. Sp. gr. 1·98 at 17°. (Guthrie.) Boils at 108° (Guthrie); between 104° and 105°. (Cahours.) It fumes strongly in the air, has a very pungent odour, and intensely sour caustic taste. (Guthrie.)

| | | | | Guthrie. |
|---|---|---|---|---|
| 4 C | 24 | 14·12 | | 15·39 |
| 3 H | 3 | 1·76 | | 2·33 |
| I | 127 | 74·71 | | 73·68 |
| 2 O | 16 | 9·41 | | 8·60 |
| $C^4H^3O^2I$ | 170 | 100·00 | | 100·00 |

The excess of carbon and hydrogen in the analysis arose from admixture of anhydrous acetic acid.

*Decompositions.* 1. Iodide of acetyl is partially decomposed by distillation (*vid. sup.*). — 2. Water decomposes it instantly and with violence, forming hydriodic and acetic acids. (Guthrie, Cahours.) — 3. It acts violently on alcohol, forming acetate of ethyl. (Cahours.) — 4. It is decomposed by zinc and by sodium at ordinary temperatures, also by

mercury in direct sunshine, iodide of mercury being formed and little or no permanent gas given off. The products formed by the action of these three metals on iodide of ethyl are similar, and consist of one or of a number of bodies, which are soluble in ether, and in contact with the air quickly absorb oxygen and become hardened. (Guthrie.)

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## Bromacetic Acid. $C^4H^3BrO^4$.

W. H. Perkin & B. F. Duppa. *Chem. Soc. Qu. J.* xi, 22.

*Formation.* By the action of bromine on acetic acid:

$$C^4H^4O^4 + 2Br = C^4H^3BrO^4 + HBr.$$

A small quantity of bibromacetic acid is formed at the same time.

*Preparation.* A mixture of glacial acetic acid and bromine in equal numbers of atoms (an excess of acetic acid being used to absorb the hydrobromic acid and thereby diminish the pressure) is introduced into a strong sealed tube, and heated in an oil-bath to 150°, and the bath is then left to cool gradually. When the temperature has fallen to about 146°, the mixture suddenly becomes nearly colourless or light amber brown, and at the same time the tubes are apt to burst, though the temperature of the bath may have risen as high as 155°. The tube when quite cold is opened, torrents of hydrobromic acid gas then escaping; the contents are transferred to a retort provided with proper apparatus for condensing the hydrobromic acid, and heated to 200°; and the retort is left to cool. The whole contents then solidify after a while into a beautifully crystalline mass consisting of bromacetic and bibromacetic acids, mixed with hydrobromic acid, to remove which the mixture is heated to 130°, and carbonic acid gas passed through it till the presence of hydrobromic acid is no longer indicated by nitrate of silver. Carbonate of lead is then added in excess, together with a volume of water about ten times as great as that of the acid; and the whole is heated to 100°, and allowed to stand for some hours. Bromacetate of lead then crystallises out, while the bibromacetate remains in solution; the crystals may be freed from the last portions of this salt by washing with a little cold water. Lastly, the crystals of bromacetate of lead are suspended in water and decomposed by sulphuretted hydrogen, and the filtered liquid is evaporated till it crystallises.

*Properties.* Bromacetic acid forms rhombohedral crystals which are very deliquescent. Melts below 100°, and boils at 208°. Attacks the skin powerfully, raising a blister like a burn; when the acid is dilute, this effect takes place after eight or ten hours only.

*Decompositions.* 1. The acid strongly heated in a sealed tube, is resolved into bibromacetic acid, carbonic oxide, and apparently marsh-gas, together with water and hydrobromic acid, probably as represented by the equation:

$$3C^4H^3BrO^4 = C^4H^2Br^2O^4 + 6CO + C^2H^4 + HBr + 2HO.$$

2. On distilling it with acetate of potash, acetic acid is evolved. —
3. Heated with metallic zinc, it yields acetate and bromide of zinc. —
4. Heated with ammonia, it forms bromide of ammonium and glycocol:

$$C^4BrH^3O^4 + 2NH^3 = NH^4Br + C^4NH^5O^4.$$

*Combinations.* The acid dissolves very readily in *water.*

With most bases it forms crystallisable salts, many of which decompose rapidly.

*Bromacetate of Ammonia.* — Nearly uncrystallisable, very soluble in water; decomposes when heated, yielding bromide of ammonium.

*Bromacetate of Potash.* — Obtained by neutralising a solution of carbonate or hydrate of potash with bromacetic acid, and evaporating the solution in a water-bath. It is a crystalline salt very soluble in water and alcohol.

*Bromacetate of Soda* is very soluble in water, but insoluble, or nearly so in alcohol.

*Bromacetate of Baryta* crystallises with difficulty in small stars, containing water of crystallisation; it is tolerably soluble in alcohol.

*Bromacetate of Lime* is a very difficult crystallisable salt, very soluble in water.

*Bromacetate of Copper* is a green crystalline salt, very soluble in water. A solution of it appears to decompose when boiled, as the colour becomes paler. The solution, after standing for some days, deposits needle-shaped crystals and small malachite-green tufts of great beauty, which appear to contain a large quantity of water of crystallisation.

*Bromacetate of Lead.* — Obtained, either by neutralising bromacetic acid with oxide of lead and recrystallising the product from water, or by adding a solution of bromacetic acid to a solution of acetate of lead, washing the resulting crystalline precipitate with cold water, and recrystallising from water. Crystallises in needles sparingly soluble in cold, but moderately soluble in hot water.

| | *At* 100°. | | Perkin & Duppa. |
|---|---|---|---|
| 4 C | 24·0 | 9·9 | 10·25 |
| 2 H | 2·0 | 0·8 | 0·9 |
| Br | 80·0 | 33·1 | 33·1 |
| Pb | 103·6 | 42·9 | 42·8 |
| 4 O | 32·0 | 13·3 | |
| $C^4BrH^2PbO^4$ | 241·6 | 100·0 | |

*Bromacetate of Silver.* — $C^4BrH^2AgO^4$. — Obtained by treating bromacetic acid with carbonate of silver, or by adding a solution of bromacetic acid to a solution of nitrate of silver. In the latter case, it is thrown down as a beautiful crystalline precipitate, which may be washed with cold water, and dried over sulphuric acid in vacuo. Contains 43·62 p. c. silver (by calculation, 43·9).

It is very unstable. The dry salt heated to about 90°, decomposes with a sort of an explosion. It is rapidly acted upon by light when moist. Boiled with water, it yields bromide of silver and glycolic acid:

$$C^4BrH^2AgO^4 + 2HO = AgBr + C^4H^4O^6.$$

*Bromacetate of Methyl.* — $C^6H^5BrO^4 = C^2H^3O,C^4H^2BrO^3$. — Obtained by heating a mixture of methylic alcohol and bromacetic acid in a sealed tube for an hour, to a temperature of 100°, washing the product with water, drying over chloride of calcium, and rectifying.

Transparent, colourless, mobile liquid, having an aromatic odour highly irritating both to the nose and the eyes. It is heavier than water; boils at about 144°, decomposing gradually every time it is distilled. Ammonia acts on it very readily.

*Bromacetate of Ethyl.* — $C^8H^7BrO^4 = C^4H^5O,C^4H^2BrO^3$. — Obtained in a similar manner to the preceding. It is a clear colourless liquid, heavier than water, and highly irritating to the eyes and nose. It boils at 159°.

| | | | Perkin & Duppa. |
|---|---|---|---|
| 8 C | 48 | 28·7 | 28·0 |
| 7 H | 7 | 4·2 | 3·5 |
| Br | 80 | 47·7 | 47·5 |
| 4 O | 32 | 19·4 | 21·0 |
| $C^8H^7BrO^4$ | 167 | 100·0 | 100·0 |

Decomposes partially every time it is distilled, with evolution of hydrobromic acid. It is rapidly acted on by ammonia.

*Bromacetate of Amyl.* — $C^{14}H^{13}BrO^4 = C^{10}H^{11}O,C^4H^2BrO^3$. — Obtained by heating amylic alcohol with excess of bromacetic acid, washing the product with water, and drying over chloride of calcium. It is an oily liquid which has a pleasant odour when cold, but if heated, acts upon the eyes and nose like the preceding. It boils at 207°, and decomposes partially every time it is distilled. Ammonia acts but slowly upon it in the cold.

| | | | Perkin & Duppa. |
|---|---|---|---|
| 14 C | 84 | 40·19 | 40·02 |
| 13 H | 13 | 6·22 | 5·28 |
| Br | 80 | 38·22 | |
| 4 O | 32 | 15·37 | |
| $C^{14}H^{13}BrO^4$ | 209 | 100·00 | |

The bromacetates of methyl, ethyl, and amyl boil at temperatures about 82° to 86°, higher than the acetates. Thus —

| | Boiling point. | | Boiling point. | Diff. |
|---|---|---|---|---|
| Bromacetate of Methyl | 144° | Acetate of Methyl | 58° | 86° |
| ,, Ethyl | 159° | ,, Ethyl | 74° | 85 |
| ,, Amyl | 207° | ,, Amyl | 125° | 82° |

A similar difference exists between the boiling points of bromacetic acid (208°), and acetic acid (120°).

## Bibromacetic Acid. $C^4H^2Br^2O^4$.

PERKIN & DUPPA. *Chem. Soc. Qu. J.* xi, 28.

This acid is formed when a mixture of bromine and acetic acid is heated in presence of light; also in small quantities when bromacetic acid is heated. It is difficult to obtain in large quantities.

Bibromacetic acid is a very heavy liquid, boiling at about 240°; it is decomposed partially every time it is distilled, evolving hydrobromic acid. It does not solidify at 15°. It is possible that by the continued action of heat it might be transformed into terbromacetic acid. Its specific gravity is very great.

Bromacetic acid forms salts with most bases, which are in general uncrystallisable.

*Bibromacetate of Baryta* is deliquescent, drying up to a gum-like sticky mass.

*Bibromacetate of Lead* is uncrystallisable, drying up to a highly refractive transparent substance, which attracts moisture and becomes opaque. It is very soluble in water.

*Bibromacetate of Silver* is obtained as a crystalline precipitate by adding nitrate of silver to a solution of bibromacetic acid. By boiling with water it is resolved into bromide of silver and a soluble acid.

| | | | Perkin & Duppa. |
|---|---|---|---|
| 4 C | 24 | 7·4 | |
| H | 1 | 0·2 | |
| Ag | 108 | 33·2 | 38·1 |
| 2 Br | 160 | 49·3 | 49·1 |
| 4 O | 32 | 9·9 | |
| $C^4Br^2HAgO^4$ | 325 | 100·0 | |

*Bibromacetate of Ethyl* is obtained by heating alcohol with bibromacetic acid to 100° in a sealed tube, washing the product with water, and drying over sulphate of copper.

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## Action of Chlorine on Aldehyde.

A. WURTZ. *N. Ann. Chim. Phys.* 49, 58.

Perfectly dry aldehyde introduced into a large vessel filled with dry chlorine, is immediately attacked and begins to boil, and in a few hours the colour of the chlorine disappears entirely. The product begins to boil at 50°, and the boiling point ultimately reaches 200°. The more volatile portion consists chiefly of chloride of acetyl $C^4H^3O^2Cl$, and is decomposed by water into hydrochloric and acetic acids.

*Monochlorometaldehyde*, $C^8H^7ClO^4$. — On collecting apart the liquid which passes over at 120°, and washing it repeatedly with water, a dense oil is obtained, which when dehydrated by chloride of calcium, distils between 120° and 130°, and appears to consist of a double molecule of aldehyde, in which 1 At. H. is replaced by chlorine.

| | | | Wurtz. |
|---|---|---|---|
| 8 C | 48·0 | 39·17 | 39·00 |
| 7 H | 7·0 | 5·71 | 6·04 |
| Cl | 35·5 | 28·97 | 26·87 |
| 4 O | 32·0 | 26·15 | 28·09 |
| $C^8H^7ClO^4$ | 122·5 | 100·00 | 100·00 |

Chloral is not found among the products of the reaction.

## Monochlorinated Chloride of Acetyl. $C^4H^2Cl^2O^2$.

WURTZ. *N. Ann. Chim. Phys.* 49, 60.

When chloride of acetyl is introduced into large flasks filled with dry chlorine, the colour of the gas disappears rapidly in sunshine, and after 24 hours in diffused daylight. On opening the vessel, acid vapours are given off in considerable quantity and with great force, indicating the formation of gaseous or very volatile products. The resulting liquid begins to boil at 55°, the boiling point ultimately rising to 200°; and by repeated fractional distillation, monochlorinated chloride of acetyl is obtained, boiling between 100° and 105°.

Colourless liquid, having an irritating odour, and diffusing a small quantity of white acid vapours in the air. Sp. gr. 1·495 at 0°. Boils at about 105°.

| | | | Wurtz. | |
|---|---|---|---|---|
| 4 C | 24 | 21·23 | 21·07 | |
| 2 H | 2 | 1·76 | 1·71 | |
| 2 Cl | 71 | 62·83 | 63·70 | 62·77 |
| 2 O | 16 | 14·18 | 13·52 | |
| $C^4H^2Cl^2O^2$ | 113 | 100·00 | 100·00 | |

The compound is decomposed by water, yielding hydrochloric and monochloracetic acids:

$$C^4H^2Cl^2O^2 + 2HO = HCl + C^4H^3ClO^4.$$

It absorbs dry ammonia with avidity, yielding sal-ammoniac and monochloracetamide. Alcohol converts it, with evolution of heat, into hydrochloric acid and monochloracetate of ethyl.

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## Monochloracetic Acid.

R. HOFFMANN. *Ann. Pharm.* 102, 1.

Dumas observed that in the preparation of terchloracetic acid by the action of chlorine on acetic acid in sunshine, a lower substitution product is always obtained, especially if the acetic acid is in excess, in the form of an uncrystallisable acid, which however he did not succeed in preparing in the separate state. F. Leblanc afterwards obtained this acid, the monochloracetic acid, in the form of a colourless liquid, by passing chlorine through glacial acetic acid in the shade; his product however was not quite pure. More recently Hoffmann has shown that the chief product of the action of chlorine on acetic acid in sunshine, is not terchloracetic but monochloracetic acid, and that this acid when pure is solid and crystalline at ordinary temperatures.

*Preparation.* 1. A tubulated retort of about 1 litre capacity and containing from half a pound to a pound of glacial acetic acid, is placed in a bath containing a saturated solution of nitrate of soda (boiling at 120°), and dry chlorine gas is passed into the retort by a tube passing through the tubulure and terminating just above the liquid, so that the gas may mix immediately with the vapour of the acid. The neck of the retort, having a wide glass tube attached to it, is directed upwards, so that any acetic acid which evaporates undecomposed may be condensed and flow back again, while the hydrochloric acid and excess of chlorine escape. The whole apparatus is placed in the sunshine, and the evolution of chlorine is so regulated that the upper part of the retort always appears coloured by it. The stronger the light, the more rapid is the absorption of chlorine; but the action takes place, though slowly, even under a clouded sky. A very slow substitution of chlorine for hydrogen likewise takes place in the dark and at ordinary temperatures. As the formation of chloracetic acid goes on, the action slackens, so that it is best, after about 15 hours' exposure to sunshine, or twice as long to diffused daylight, to expel the excess of chlorine from the apparatus by a stream of dry air, and rectify the product in a smaller retort. The portion which distils below 130°, consists almost wholly of unaltered acetic acid, and may be used in a subsequent preparation. That which passes over between 130° and 190°, is easily separated by repeated rectification into acetic acid and a thick liquid which boils between 185° and 187° and either solidifies immediately into a mass of white needle-shaped crystals, or yields after some time, large, isolated, transparent, colourless, rhombic tables, while the greater portion remains liquid, but if shaken up or stirred with a glass rod, solidifies suddenly and with considerable rise of temperature, the crystals previously formed becoming opaque and white like porcelain. The crystalline mass, which melts between 45° and 47°, consists of nearly pure monochloracetic acid, mixed however with a certain quantity of liquid, which may be removed by decantation and rapid pressure, and used, together with the portion of the original liquid which distilled below 130°, in a subsequent preparation. The expressed crystals are placed on bibulous paper and completely dried in vacuo over oil of vitriol and a few lumps of hydrate of potash, and then redistilled, the first and last portions of the distillate being rejected. As they are very deliquescent, they should be kept as much as possible from the air. (Hoffmann.)

In the first distillation, and in the subsequent rectifications, there is obtained a small quantity of a liquid which boils above 190°, and appears to contain an acetic acid with more than 1 At. hydrogen replaced by chlorine. It yielded in different experiments, from 48 to 50 per cent. of chlorine, which does not agree with the formula either of bichloracetic (requiring 55·04) or of terchloracetic acid (requiring 65·13 p. c. of chlorine). In one experiment, this liquid, on being saturated with baryta, yielded, besides monochloracetate of baryta, a small quantity of small opaque warty crystals, the composition of which seemed to show that they contained a higher chlorinated acid; but in no instance, even when the purest crystallised acetic acid was used and the absorption took place in the brightest sunshine, was any definite bichloracetic or terchloracetic obtained, the chief product being invariably monochloracetic acid. Neither was any oxalic acid formed, as stated by Dumas (ix, 209). (Hoffmann.)

2. Monochloracetic acid is also obtained in a state of purity by the action of water on monochlorinated chloride of acetyl. On distilling the liquid, the thermometer rises from 100° to 180°, and the liquid which passes over at that temperature solidifies in a crystalline mass on cooling. (Wurtz, p. 536).

*Properties.* Crystallises from fusion in rhombic tables, having acute angles of 77° or 78°; from solution in acetic acid—*e. g.*, from the liquids obtained in the first distillation between 180° and 186° and between 186° and 190°, — in crystals having a prismatic character, and very much resembling those of terchloracetic acid. Melting point 62°. When the melted acid was left to cool, the thermometer at the commencement of crystallisation generally marked 60°, then rose rapidly to 63° or 64°, and ultimately sank to 62°, at which point it remained constant. It contracts strongly in solidifying, and generally gives off numerous air-bubbles. The specific gravity of the melted acid at 73°, is 1·366 as compared with water at 19°, and 1·3947 compared with water at 73°. Boiling point from 185° to 187·8°. It distils undecomposed, and when pure solidifies in the neck of the retort; but if mixed with acetic acid, remains liquid below its ordinary point of solidification. When kept for some time at a temperature near its melting point, it sublimes in long spicular crystals. It is nearly inodorous at ordinary temperatures, but its vapour has a pungent suffocating odour. It has a strong acid taste, attacks the cuticle, and raises blisters if kept on it for some time.

| | | | Hoffmann. |
|---|---|---|---|
| 4 C | 24·0 | 25·40 | 25·27 |
| 3 H | 3·0 | 3·17 | 3·29 |
| Cl | 35·5 | 37·57 | 37·64 to 39·6 |
| 4 O | 32·0 | 33·86 | |
| $C^4H^3ClO^4$ | 94·5 | 100·00 | |

*Decompositions.* 1. The acid is decomposed by pentachloride of phosphorus, with formation of chlorophosphoric acid and monochlorinated chloride of acetyl; but the two chlorides cannot be separated by distillation, as they both boil at about 110°. When the product was repeatedly distilled with small portions of acid monochloracetate of potash, the residues of the last distillations yielded at high temperatures a large proportion of monochloracetic acid, the last portions of which boiled as high as 200°, and had a more penetrating odour, probably arising from the presence of a small quantity of the anhydrous acid. — 2. The acid heated with potash-ley, ammonia, baryta-water, or lime-water, immediately yields a chloride of the alkali-metal without any carbonic, formic, oxalic, or acetic acid. In this respect, it differs remarkably from acetic and from terchloracetic acid (viii, 295; ix, 211); after boiling for

some time the whole of the monochloracetate is decomposed. A similar but less complete decomposition takes place when a neutral solution of a monochloracetate, or even the free acid, is boiled for a considerable time. The crystallised potash-salt also is decomposed in like manner at 110°, becoming dull and yellowish, and acquiring an acid reaction; cold water then extracts from it chloride of potassium, and leaves a white powder, which has an acid reaction, dissolves in hot water, and separates on cooling. Possibly the reaction may consist in the formation of a metallic chloride and the assumption of the elements of water by the organic residue, the result of which will be the formation of a compound having the composition of glycolic acid:

$$C^4H^2ClMO^4 + 2HO = C^4H^4O^6 + MCl.$$

3. Monochloracetic acid is reduced by potassium or sodium-amalgam, to acetic acid, in the same manner as terchloracetic acid (ix, 211); the decomposition is however incomplete, and is attended with evolution of hydrogen. (Hoffmann.)

*Combinations.* The acid deliquesces in the air, and dissolves very easily in *water*, producing considerable fall of temperature.

The *Monochloracetates*, $C^4Cl^2MO^4$, are obtained by digesting the oxides or carbonates in the aqueous acid: they are for the most part easily soluble and crystallisable.

*Monochloracetate of Ammonia* decomposes by evaporation like the potash-salt. It is more soluble than that salt, and solidifies only from a perfectly viscid solution, in the form of a crystalline cake, which quickly deliquesces on exposure to the air. The salt was not obtained free from sal-ammoniac.

*Monochloracetate of Potash.* — *a. Neutral*, $C^4ClH^2KO^4 + 3Aq.$ — Obtained by saturating the acid with carbonate of potash and evaporating to a syrup in vacuo over oil of vitriol. It then separates in thin colourless laminæ, which may be obtained pure by draining on bibulous paper. It is not deliquescent, and does not give up its water of crystallisation at 100°, but is decomposed at a higher temperature, yielding chloride of potassium (p. 538), also when its solution is evaporated at a gentle heat. It is very soluble in water. After drying in vacuo, it yielded 24·63 p. c. potassium (by calculation, 24·55).

*b. Acid.* $C^4ClH^2KO^4,C^4ClH^2O^4$. — When a solution of the neutral salt is mixed with as much acid as it already contains, the whole solidifies to a thick pulp of small white pearly crystals, which may be purified by draining on bibulous paper or by drying over oil of vitriol. Sparingly soluble in water. Contains 17·23 p. c. potassium (by calculation, 17·25).

*Monochloracetate of Baryta*, $C^4ClH^2BaO^4 + 2Aq.$ — May be obtained, even with very small quantities of material, in distinct prismatic crystals, apparently belonging to the rhombic system, and containing 39·99 p. c. barium (by calculation 40·06). Decomposes but little during evaporation, and separates out almost completely on cooling from a hot saturated solution. (Hoffmann.)

*Monochloracetate of Silver.* — A hot solution of the acid saturated with oxide of silver, yields the salt on cooling in splendid rhomboidal, iridescent laminæ. (Wurtz.) — Anhydrous. Dissolves sparingly in cold,

more readily in hot water, and is easily obtained by cooling in small nacreous scales which blacken on exposure to light and yield chloride of silver. Between 110° and 120° it decomposes with a kind of explosion, emitting the same odour as the acid when it evaporates, and leaving chloride of silver mixed with a very small quantity of metallic silver. (Hoffmann.)

| | | | Wurtz. | Hofmann. |
|---|---|---|---|---|
| 4 C | 24·0 | 11·91 | 11·91 | |
| 2 H | 2·0 | 0·99 | 1·07 | |
| Cl | 35·5 | 17·61 | 17·48 | |
| Ag | 108·0 | 53·59 | 53·41 | 52·03 |
| 4 O | 32·0 | 15·90 | 16·13 | |
| $C^4ClH^2AgO^4$ | 201·0 | 100·00 | 100·00 | |

## Monochloracetate of Ethyl.

$C^8ClH^7O^4 = C^4H^5O,C^4ClH^2O^3$.

E. Willm. *N. Ann. Chim. Phys.* 49, 97.

Obtained by the action of alcohol on monochlorinated chloride of acetyl:

$$C^4H^6O^2 + C^4Cl^2H^2O^2 = C^8ClH^7O^4 + HCl.$$

The action, which is very violent, must be moderated by cooling the vessel externally, and, as soon as it is finished, the product may be washed with water, dehydrated by chloride of calcium and rectified.

Colourless liquid, having an ethereal odour and burning taste, heavier than water and insoluble in that liquid. Boils at 143·5° when the barometer stands at 758° mm. Vapour-density 4·46.

| | | | Willm. |
|---|---|---|---|
| 8 C | 48·0 | 39·19 | 38·87 |
| 7 H | 7·0 | 5·72 | 5·87 |
| Cl | 35·5 | 28·95 | 29·03 |
| 4 O | 32·0 | 26·14 | 26·20 |
| $C^8H^7ClO^4$ | 122·5 | 100·00 | 100·00 |

| | Vol. | Density. |
|---|---|---|
| C-vapour | 8 | 3·3280 |
| H-gas | 7 | 0·4851 |
| Cl-gas | 1 | 2·4543 |
| O-gas | 2 | 2·2186 |
| Vapour of $C^8H^7ClO^4$ | 2 | 8·4860 |
| | 1 | 4·2430 |

The ether burns with a bright flame, green at the edges. It is decomposed by potash, into alcohol and monochloracetic acid, which then suffers further decomposition, yielding chloride of potassium and acetate of potash.

It is insoluble in water.

## Monochloracetamide.

$C^4H^4ClNO^2 = C^4ClAdH^2,O^2 = N.H^2,C^4ClH^2O^2.$

E. WILLM. *N. Ann. Chim. Phys.* 49, 99.

Obtained: 1. By the action of ammonia on monochloracetate of ethyl:

$$C^8H^7ClO^4 + NH^3 = C^4H^4ClNO^2 + C^4H^6O^2.$$

2. By bringing perfectly dry ammoniacal gas in contact with monochlorinated chloride of acetyl:

$$C^4H^3Cl^2O^2 + 2NH^3 = C^4H^4ClNO^2 + NH^4Cl.$$

The product is a white amorphous mass, from which absolute alcohol extracts the monochloracetamide and leaves sal-ammoniac. On evaporating the alcoholic solution, the amide is obtained in large shining laminæ. It dissolves in 10 parts of water at 24°, and in 10½ pts. of alcohol at the same temperature, but is very sparingly soluble in ether. From the aqueous solution it crystallises by evaporation in small mammellated masses.

| | | | | Willm. |
|---|---|---|---|---|
| 4 C | 24·0 | 25·67 | | 25·75 |
| 4 H | 4·0 | 4·30 | | 4·70 |
| Cl | 35·5 | 37·95 | | 38·29 |
| N | 14·0 | 14·88 | | |
| 2 O | 16·0 | 17·20 | | |
| $C^4H^4ClNO^2$ | 93·5 | 100·00 | | |

It is decomposed by potash, with evolution of ammonia, and formation of chloride of potassium and acetate of potash.

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## Acetosylamine.

$C^4H^5N = C^4H^3,H^2N.$

J. NATANSON. *Ann. Pharm.* 98, 291.

***Acetylamine.***

Produced by the distillation of hydrated oxide of acetosylium (or acetylium, x, 538):

$$\left.\begin{matrix}C^4H^3\\H^3\end{matrix}\right\}NO,HO = C^4H^3,H^2N + 2HO.$$

*Preparation.* The yellow liquid obtained by the action of ammonia on chloride of ethylene is evaporated till the sal-ammoniac crystallises

out; the mother-liquor separated from the crystals is mixed with excess of hydrate of baryta and evaporated to dryness; the dry residue is exhausted with absolute alcohol; the alcohol distilled off from the extract and afterwards the water; and the residue is heated to between 150° and 200°. Acetosylamine then passes over in yellowish oily drops, which may be purified by rectification, the portion which distils between 210° and 220° being collected apart.

*Properties.* Liquid having a faint yellow colour (probably colourless when quite pure). Sp. gr. 0·975 at 15°. Does not solidify at —15°. Has an ammoniacal and very persistent odour, resembling that of aldehyde-ammonia at ordinary temperatures and that of aniline at the boiling heat. Its taste is caustic. The aqueous solution blues red litmus strongly; the dry base does not. Boils at 218°. Vapour-density 1·522. The vapour burns with a whitish blue flame.

| | | | | Natanson. | | Vol. | Density. |
|---|---|---|---|---|---|---|---|
| 4 C | 24 | 55·81 | 55·97 | C-vapour | 4 | 1·6640 |
| 5 H | 5 | 11·63 | 11·31 | H-gas | 5 | 0·3465 |
| N | 14 | 32 56 | 32·26 | N-gas | 1 | 0·9706 |
| $C^4H^5N$ | 43 | 100·00 | 100·00 | Vapour of $C^4H^5N$ | 2 | 2·9811 |
| | | | | | 1 | 1·4905 |

Ammonia in which 1 At. H is replaced by acetosyl $C^4H^3$.

Acetosylamine is not decomposed by sodium. When heated with iodide of ethyl, it yields apparently the hydriodate of ethylacetosylamine. $(C^4H^3)(C^4H^5)HN$. The product decomposed by potash yields a brown oil possessing basic properties.

*Combinations.* Acetosylamine mixes in all proportions with *water*.

It combines with *acids*, forming salts which exhibit all the characters of the salts of acetosylium. It absorbs water and carbonic acid when exposed to the air. A glass rod moistened with it, fumes when held over hydrochloric acid. The salts of acetosylamine when decomposed by potash, do not give off the characteristic odour of the base, because it is then converted into the inodorous oxide of acetosylium; the aqueous solution however, retains the odour for a long time. Heated with chloride of lime, or with chromate of potash and sulphuric acid, they give off a considerable quantity of aldehyde.

Acetosylamine forms precipitates with most metallic solutions.

The *Platinum-salt*, $C^4H^8NCl,PtCl^2$, is an orange-yellow amorphous powder sparingly soluble in cold, easily in hot water. It gave by analysis 39·29, 39·34 and 39·86 p. c. platinum, (compare x, 540).

Acetosylamine mixes in all proportions with *alcohol*, but is insoluble in ether.

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*Preparation of Acetamide and Acetonitrile.*—Acetamide is readily obtained by heating a mixture of equal volumes of acetate of ethyl and strong aqueous ammonia to a temperature between 120° and 130° in a closed vessel for six hours. On subsequently distilling the product, that which passes over above 260° is pure acetamide. (Buckton & Hofmann, *Chem. Soc. Qr. J.* 9, 242).

When acetamide is mixed with about an equal volume of anhydrous phosphoric acid, a violent action takes place, and acetonitrile passes over, contaminated however with hydrocyanic and acetic acids. The distillate is washed with potash, and the acetonitrile is decanted and rectified over anhydrous phosphoric acid. Thus prepared it has an ethereal odour, somewhat like that of cyanogen, and a rather pungent, aromatic taste; it boils at 77° or 78°, and burns with a bright flame reddish at the edges. (Buckton & Hofmann.)

*Preparation of Acetamide from Acetate of Ammonia.*— It is generally supposed that the ammonia-salts of monobasic acids do not yield amides by dehydration. Kündig has however shown (*Ann. Pharm.* 105, 277) that when acetate of ammonia is distilled, a portion of it is converted into acetamide. At the beginning of the distillation, a large quantity of ammonia is given off; afterwards at 160°, at which point the thermometer remains constant for a long time, an acid distillate, probably consisting of acid acetate of ammonia; above 160° a distillate containing acetamide, which at a temperature a little higher, crystallises in the condensing tube; and above 190° nearly pure acetamide. The quantity of that substance is not increased by addition of alcohol. The largest product is obtained by passing dry ammoniacal gas for some hours through glacial acetic acid, which is at first kept cool in an apparatus provided with a condensing tube directed upwards, but afterwards heated to commencing ebullition. By subsequent distillation, a quantity of acetamide was obtained equal to ¼ that of the glacial acetic acid used.

In the distillations above described, the thermometer was never observed to rise above 218°; neither, according to Kündig does it ever rise above that point, in the preparation of acetamide by the action of ammonia on acetic ether, whereas Buckton & Hofmann state that the portion which distils above 260° is to be regarded as pure acetamide. The boiling point of pure acetamide was found by Kündig to be 222°, attention being paid to the corrections pointed out by Kopp (*Ann. Pharm.* 94, 259).

## Compounds of Acetamide.

STRECKER. *Ann. Pharm.* 103, 321.

*Hydrochlorate.* — $(C^4H^5NO^2)^2,HCl$. — Obtained: 1. By the action of chlorophosphoric acid on acetamide. When chlorophosphoric acid is added to acetamide fused at a gentle heat, the two liquids mix, producing rise of temperature, and soon solidify into a compact mass, without evolution of hydrochloric acid or any other gas. This mass is insoluble in anhydrous ether, but absolute alcohol dissolves it, especially with the aid of heat; and the solution on cooling, or better on addition of ether, deposits colourless crystalline needles of hydrochlorate of acetamide. The crystalline mass at first obtained appears to be a compound of acetamide with chlorophosphoric acid, which, on addition of alcohol, is resolved into phosphoric ether and hydrochloric acid, the latter uniting with the acetamide:

$$[2C^4H^5NO^2 + PCl^3O^2 + 3\left(\begin{matrix}C^4H^5\\H\end{matrix}O^2\right) = (C^4H^5NO^2)^2HCl + P(C^4H^5)^3O^8 + 2HCl].$$

2. By the action of hydrochloric acid gas on a solution of acetamide in ether-alcohol, the liquid being cooled from without and the gas directed on its surface. The greater part of the liquid then solidifies in a crystalline mass, which is washed with anhydrous ether and dissolved in warm alcohol; the solution on cooling, or more quickly on addition of ether, yields the hydrochlorate in the crystalline form. This mode of preparation is preferable to the former.

*Properties.* Long spear-shaped crystals, which dissolve readily in water and alcohol, but are insoluble in ether. They have a very sour taste and an acid reaction.

| | | | Strecker. |
|---|---|---|---|
| 8 C | 48·0 | 31·1 | |
| 12 H | 11·0 | 7·1 | |
| 2 N | 28·0 | 18·1 | 18·2 |
| Cl | 35·5 | 23·0 | 22·9 |
| 4 O | 32·0 | 20·7 | |
| $(C^4H^5NO^2)^2HCl$ | 154·5 | 100·0 | |

The alcoholic solution of the crystals does not form any precipitate with bichloride of platinum, but after standing for some time in the cold, and quickly when heated, it deposits chloroplatinate of ammonium, giving off at the same time an odour of acetic ether.

Perfectly dry hydrochlorate of acetamide heated in a sealed tube, melts at first without decomposition, but between 180° and 200°, it suffers complete decomposition, being converted into a pasty mixture of solid and liquid matter, which, when distilled in the oil-bath, yielded first a strongly acid liquid (*a*), and afterwards a liquid which solidified in colourless crystals (*b*) in the receiver, while a slightly brown residue (*c*) remained in the retort. The same products are obtained when acetamide is heated in a stream of dry hydrochloric gas. — *a*. The first distillate when rectified begins to boil at 60°, at which temperature *chloride of acetyl* and apparently also acetonitrile pass over, the boiling point afterwards rising to 120°, and concentrated *acetic acid* passing over. — *b*. The crystalline distillate dissolves partly in ether, the undissolved portion consisting of unaltered hydrochlorate of acetamide, and the ethereal solution yielding on evaporation over sulphuric acid, crystalline granules of a compound of acetamide and biacetamide, $C^{12}H^{12}N^2O^6 = C^4H^5NO^2 + C^8H^7NO^4$. — The non-volatile residue in the retort is partially soluble in alcohol, the undissolved portion consisting of sal-ammoniac, and the alcoholic solution depositing by spontaneous evaporation crystals of *hydrochlorate of acediamine* $C^4H^6N^2,HCl$.

The decomposition of hydrochlorate of acetamide by heat, or of acetamide under the influence of heat and dry hydrochloric acid, may be represented by the following equations:

$$2C^4H^5NO^2 + HCl = \underbrace{C^8H^7NO^4}_{\text{biacetamide.}} + NH^4Cl.$$

$$2C^4H^5NO^2 + HCl = \underbrace{C^4H^6N^2,HCl}_{\text{hydrochlorate of acediamine}} + \underbrace{C^4H^4O^4}_{\text{acetic acid.}}$$

$$C^4H^5NO^2 + 2HCl = \underbrace{C^4H^3O^2Cl}_{\text{chloride of acetyl.}} + NH^4Cl.$$

$$C^4H^5NO^2 = \underbrace{C^4H^3N}_{\text{acetonitrile.}} + 2HO.$$

*Nitrate of Acetamide.* — $C^4H^5NO^2,HNO^6$. — When acetamide is dissolved in cold strong nitric acid, and the solution is left exposed to the air in shallow vessels, colourless crystals separate, which have a very sour taste and reaction, even after being dried between bibulous paper. They melt at a moderate heat, and detonate when more strongly heated in a test-tube, leaving scarcely any residue. They gave by analysis 45·2 p. c. nitric acid, the formula requiring 44·2. The excess arose from adhering nitric acid.

*Acetamidate of Mercury,* $C^4H^4HgNO^2$. — Yellow mercuric oxide added to a solution of acetamide disappears very quickly at first; but for complete saturation, it is necessary, towards the end of the process, to heat the liquid with excess of mercuric oxide. The filtered solution evaporated in vacuo leaves colourless crystalline crusts, easily soluble in water, sparingly in alcohol. The crystals, after drying in the air, did not lose so much as 1 p. c. at 100°. They gave by analysis 62·8 p. c. mercury (calculation 63·3).

The aqueous solution of the crystals does not form any precipitate with potash at ordinary temperatures, but deposits white flakes on boiling. Ammonia, on the other hand, immediately produces a yellowish turbidity, which increases considerably on boiling. Metallic zinc immersed in the aqueous solution becomes covered with a grey film of mercury, white flakes of oxide of zinc floating in the liquid. The liquid after a while contains neither mercury nor zinc in solution, but when evaporated in vacuo leaves pure acetamide. Cadmium acts in a similar manner to zinc. Copper does not precipitate the mercury till the solution is acidulated.

*Acetamidate of Silver.* — Recently precipitated oxide of silver dissolves readily in aqueous acetamide, and the solution when evaporated leaves crystalline scales of acetamidate of silver. (Strecker.)

## Biacetamide.

$$C^8H^7NO^4 = (C^4H^3O^2)^2,HN.$$

STRECKER. *Ann. Pharm.* 103, 327.

The ethereal solution of the compound of acetamide and biacetamide (p. 544) deposits, when hydrochloric acid gas is passed through it, spicular crystals of hydrochlorate of acetamide, and the liquid filtered therefrom, yields by evaporation over sulphuric acid, needle-shaped crystals of biacetamide, easily soluble in water, alcohol and ether.

| | | | Strecker. |
|---|---|---|---|
| 8 C | 48 | 47·5 | 47·7 |
| 7 H | 7 | 6·9 | 6·9 |
| N | 14 | 13·9 | |
| 4 O | 32 | 31·7 | |
| $C^8H^7NO^4$ | 101 | 100·0 | |

The crystals boiled with acids are resolved into acetic acid and ammonia, but not so readily as acetamide.

The alcoholic solution is not decomposed by bichloride of platinum at ordinary temperatures, but after boiling for some time it deposits chloroplatinate of ammonium.

*Biacetamide with Acetamide,* $C^8H^7NO^4,C^4H^5NO^2$. — Deposited from the ethereal solution (p. 544), by evaporation over sulphuric acid, in hard crystalline grains, which are at first contaminated with acetic acid, but lose their acid reaction by standing over sulphuric acid or lime in vacuo. They fuse readily and volatilise gradually in vacuo at ordinary temperatures. They dissolve readily in water, alcohol and ether.

| | | | Strecker. |
|---|---|---|---|
| 12 C | 72 | 45·0 | 45·0 |
| 12 H | 12 | 7·5 | 7·9 |
| 2 N | 28 | 17·5 | 17·3 |
| 6 O | 48 | 30·0 | 29·8 |
| $C^{12}H^{12}NO^6$ | 160 | 100·0 | 100·0 |

## Acediamine. $C^4H^6N^2$.

STRECKER. *Ann. Pharm.* 103, 328.

*Formation* (p. 544), The prismatic crystals of hydrochlorate of acediamine which separate from the alcoholic solution of the residue left on distilling the product of the decomposition of hydrochlorate of acetamide, are freed from adhering sal-ammoniac by solution in a mixture of alcohol and ether; and on evaporating this solution in vacuo, the pure hydrochlorate of acediamine separates in crystals of the original form.

*Sulphate,* $C^4H^6N^2,HSO^4$. — Obtained by mixing the aqueous solution of the hydrochlorate with sulphate of silver, as long as any precipitate of chloride of silver is produced, concentrating the filtrate over the water-bath, and recrystallising from boiling alcohol. The salt is thereby obtained in colourless nacreous laminæ, easily soluble in water, sparingly in alcohol, even at the boiling heat, and neutral to vegetable colours. It gave by analysis 37·3 p. c. sulphuric acid (by calculation, 37·2).

*Chloroplatinate.* — The aqueous solution of the hydrochlorate is not precipitated by chloride of platinum; but the liquid when evaporated yields rather large hard yellowish red prisms of the platinum-salt, which are easily freed from adhering chloroplatinate of ammonium by solution

in alcohol. The crystals, after being dried in the air, do not give off any thing at 100°. They dissolve readily in water, less in alcohol, and not at all in a mixture of alcohol and ether.

| | | | Strecker. |
|---|---|---|---|
| 4 C | 24·0 | 9·1 | 9·6 |
| 7 H | 7·0 | 2·7 | 2·8 |
| 2 N | 28·0 | 10·6 | 10·5 |
| Pt | 99·0 | 37·4 | 37·15 |
| 3 Cl | 106·5 | 40·2 | |
| $C^4H^6N^2,HCl,PtCl^2$ | 264·5 | 100·0 | |

Acediamine may be regarded as ammonia in which 1 At. H. is replaced by the monatomic radical $C^4H^4N$, its rational formulæ being then $\left.\begin{matrix}C^4H^4N\\H\\H\end{matrix}\right\}N$; or as a double molecule of ammonia $N^2H^6$, having 3 At. H replaced by the triatomic radical $C^4H^3$, its formula being $\left.\begin{matrix}C^4H^3\\H^3\end{matrix}\right\}N^2$. It bears the same relation to acetamide that ethylamine bears to alcohol:

$$C^4H^6O^2 + NH^3 = C^4H^7N + 2HO.$$

and:

$$C^4H^5NO^2 + NH^3 = C^4H^6N^2 + 2HO.$$

It is very unstable, and cannot be obtained in the free state. When the sulphate or hydrochlorate is heated with a stronger base, such as potash or baryta, ammonia is given off and acetic acid remains in combination with the base:

$$C^4H^6N^2 + 4HO = C^4H^4O^4 + 2NH^3.$$

The salts likewise undergo a similar decomposition when boiled with acids in excess. Thus the residue obtained by evaporating the hydrochlorate with excess of hydrochloric acid, consists chiefly of sal-ammoniac, only a small quantity of the original salt being extracted by alcohol.

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## Ternitracetonitrile.

$$C^4N^4O^{12} = C^4X^3N.$$

L. Schischkoff. *N. Ann. Chim. Phys.* 49, 323; abstr. *Compt. rend.* 45, 277; *Ann. Pharm.* 101, 215.

Produced by the action of a mixture of nitric and sulphuric acids on fulminuric acid (x, 556):

$$C^6N^3H^3O^6 + 2NO^6H = C^4N^4O^{12} + 2CO^2 + 2HO + NH^3.$$

It is a solid substance, having the appearance of camphor, and a very penetrating disagreeable odour. It melts at 41·5°, is very volatile at ordinary temperatures, but decomposes with strong detonation at 220°.

*Calculation.*

| | | |
|---|---|---|
| 4 C | 24 | 13·64 |
| 4 N | 56 | 31·82 |
| 12 O | 96 | 54·54 |
| $C^4X^3N$ | 176 | 100·00 |

Ternitracetonitrile is rapidly decomposed by water, alcohol, sulphuretted hydrogen, ammonia, the fixed alkalis, &c. With water and alcohol it yields the ammonium-salt of nitroform, $C^2X^3NH^4$ (p. 493). — Sulphuretted hydrogen converts it into *binitrammonyl.*

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*Silver-salt.* $C^4N^{10}H^{14}Ag^2O^{26} = C^4X^3N(NH^3Ag)^3O^2 + 2(NO^6,NH^4)$. — An ammoniacal solution of ternitracetonitrile mixed with nitrate of silver, forms a yellow precipitate, which dissolves readily in hot water, and crystallises in yellow needles on cooling.

| | | | Schischkoff. |
|---|---|---|---|
| 4 C | 24 | 3·99 | 4·53 |
| 14 H | 14 | 2·33 | 2·52 |
| 10 N | 140 | 23·25 | 24·95 |
| 2 Ag | 216 | 35·88 | 35·39 |
| 26 O | 208 | 34·55 | 32·61 |
| $C^4N^{10}H^{14}Ag^2O^{26}$ | 602 | 100·00 | 100·00 |

## Binitrammonyl.

$$C^4H^4N^4O^4 = C^4X^2(NH^4)N.$$

SCHISCHKOFF. *loc. cit.*
SCHISCHKOFF & ROSING. *Ann. Pharm.* 104, 250.

*Dinitrammonyl.*—Acetonitrile in which 2 At. H are replaced by $NO^4$ and the third by $NH^4$.

Produced by the action of sulphuretted hydrogen on ternitracetonitrile:

$$C^4(NO^4)^3N + 8HS = C^4(NO^4)^2(NH^4)N + 4HO + 8S.$$

Crystallises in beautiful colourless shining needles, very soluble in water, less soluble in alcohol, and nearly insoluble in ether. When suddenly heated, it takes fire and burns away. At 100° it volatilises in perceptible quantity, emitting an extremely pungent odour.

It is perfectly neutral to test-paper, but nevertheless exhibits the properties of an acid, its hydrogen being partially replaceable by metals.

It does not give off ammonia even when boiled with moderately strong potash-ley (1 pt. hydrate of potash to 2 pts. water), but the liquid solidifies on cooling into a mass, which is probably the potash-salt $C^4X^2(NH^3K)N$.

*Silver-salt,* $C^4X^2(NH^3Ag)N$. — The aqueous solution of binitrammonyl boiled with oxide of silver, yields, when filtered and cooled, a beautifully crystallised silver-salt, which explodes very readily and dissolves sparingly in cold, but abundantly in hot water.

| | | | Schischkoff & Rosing. |
|---|---|---|---|
| 4 C | 24 | 9·41 | 9·40 |
| 3 H | 3 | 1·17 | 1·18 |
| 4 N | 56 | 21·96 | 21·35 |
| Ag | 108 | 42·35 | 41·91 |
| 8 O | 64 | 25·11 | 26·16 |
| $C^4H^3N^4AgO^8$ | 255 | 100·00 | 100·00 |

*Action of strong Sulphuric acid on Binitrammonyl.* — Binitrammonyl is slowly decomposed by sulphuric acid at ordinary temperatures. On heating the mixture over the water-bath, the action is accelerated, sulphate of ammonia is formed, and an oily layer collects on the surface; and this, when separated from the lower liquid and cooled by a mixture of ice and salt, crystallises in large fine prisms, which soon melt when removed from the freezing mixture. They explode violently when heated, are insoluble in water, and dissolve very sparingly in aqueous ammonia, forming a dark yellow solution, which leaves a brown resinous substance when evaporated. The composition of the crystals is as follows:

| | | | Schischkoff & Rosing. | |
|---|---|---|---|---|
| 10 C | 60 | 30·77 | 29·73 | 28·96 |
| H | 1 | 0·51 | 0·51 | 0·57 |
| 5 N | 70 | 35·90 | | 36·6 |
| 8 O | 64 | 32·82 | | |
| $C^{10}HN^5O^8$ | 195 | 100·00 | | |

The crystals were difficult to free from the mother-liquor, the solution becoming viscid before it crystallised.

The rational formula of the compound is perhaps $Cy^3,C^4(NO^4)^2H$.

The sulphuric acid retained in solution, besides sulphate of ammonia, a body apparently identical with the preceding; it was separated from the acid liquid by agitation with ether, but was not obtained in quantity sufficient for analysis.

*Action of Potash on Binitrammonyl.* — When binitrammonyl is boiled with a very strong, nearly syrupy solution of potash, a large quantity of ammonia is given off, and a salt gradually separates in prismatic crystals, which are but sparingly soluble in the caustic potash-ley. An additional quantity of this salt separates when the liquid is left to cool after the evolution of ammonia has ceased. This salt dissolves very sparingly in cold water or alcohol, but very abundantly in those liquids at the boiling heat, and is deposited from the solutions on cooling, in shining light yellow laminæ, somewhat like those of picric acid. The salt is perfectly

neutral to test-paper, explodes by heat or by contact with strong sulphuric acid, and is decomposed by dilute acids, with evolution of gas. Its composition is as follows:

| | | | | Schischkoff & Rosing. |
|---|---|---|---|---|
| 20 C | 120 | 12·0 | | 12·58 |
| 7 H | 7 | 0·7 | | 0·85 |
| 12 N | 168 | 16·8 | | 16·90 |
| 7 K | 273 | 27·3 | | 27·42 |
| 54 O | 432 | 43·2 | | 42·25 |
| $C^{20}H^7N^{12}K^7O^{54}$ | 1000 | 100·0 | | 100·00 |

The rational formula is probably $5C^4X^2HK + 2NO^6K + 2HO$.

## Bibromonitracetonitrile.

$C^4N^2Br^2O^4 = C^4XBr^2N$.

KEKULÉ. *Ann. Pharm.* 105, 281.

*Dibromnitroacetonitril, Cyanobibromopicrin, Cyandibromopikrin.*

*Formation and Preparation.* — By the action of bromine on fulminating mercury:

$$C^4XHg^2N + 4Br = C^4XBr^2N + 2HgBr.$$

Bromine is added to fulminating mercury immersed in water, and the liquid is distilled as soon as the colour of the bromine becomes permanent. An oil then passes over having an odour like that of chloropicrin (xi, 216) and coloured in the earlier portions by excess of bromine. The latter portions of the distillate are colourless, and solidify in the condensing tube or in the receiver in colourless crystals, the formation of which is much accelerated by shaking up with cold water. The portions of the distillate which remain liquid at first, likewise yield, when shaken up with mercury, and redistilled, a colourless oil, which, after standing for some time or after slow evaporation, deposits large crystals. — The compound is likewise obtained by the action of bromine on aqueous fulminurate of potash; but its formation is then attended with copious evolution of carbonic acid.

*Properties.* Perfectly insoluble in water, but dissolves readily in alcohol and ether, and when recrystallised therefrom by evaporation, forms colourless, shining, well developed crystals, having an odour like that of chloropicrin or bromopicrin. It is extremely volatile, giving off, even at ordinary temperatures, a vapour which attacks the eyes very powerfully. It may be distilled with water, without decomposing. Melts at 50° and solidifies in the crystalline form on cooling. Begins to boil between 130° and 135°; but decomposes at the same time, turning yellow, and giving off gas-bubbles, together with brown vapours which contain some of the oxides of nitrogen, and explode when strongly heated. When boiled for some time with potash and a ferroso-ferric salt, it gives the reaction of cyanogen.

| | | | | Kekulé. |
|---|---|---|---|---|
| 4 C | 24 | 9·84 | 10·20 | 9·73 |
| 2 N | 28 | 11·47 | | |
| 2 Br | 160 | 65·58 | 63·01 | 65·90 |
| 4 O | 32 | 13·11 | | |
| $C^4XBr^2N$ | 244 | 100·00 | | |

The formula is that of fulminating mercury in which the 2Hg are replaced by 2Br.

Bibromonitracetonitrile treated with chlorine or bromine, yields an oily product which is doubtless chloropicrin or bromopicrin. Also when fulminating mercury is treated with excess of bromine, the crystals obtained are smaller in quantity in proportion to the oily liquid, than when the fulminating mercury is in excess.

*Biniodonitracetonitrile?* — When iodine is added to fulminating mercury suspended in alcohol, and the alcoholic solution evaporated, colourless crystals are formed, which contain iodine and smell like chloropicrin; they have not yet been obtained in the pure state.

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## Constitution of Fulminic Acid.

KEKULÉ. *Ann. Pharm.* 101, 200; 105, 279.
SCHISCHKOFF. *Ann. Pharm.* 101, 213.

That the fulminates contain a nitro-compound ($NO^4$, $NO^2$, &c.) is rendered highly probable, both by their mode of formation, and by their explosive properties (ix, 296). This view receives strong confirmation from the recent experiments of Kekulé and Schischkoff, which have shown: 1. That fulminating mercury, treated with chlorine, or with hypochlorite of lime, yields chloropicrin, a compound certainly containing $NO^4$ (xi, 216); and with bromine, it yields bibromonitracetonitrile $C^4XBr^2N$, or bromopicrin $C^4XBr^3$, according as the fulminating mercury or the bromine is in excess. — 2. Fulminuric or isocyanuric acid, $C^6N^3H^3O^6$, a compound produced by the action of alkaline chlorides or iodides on fulminating mercury (x, 556) also yields chloropicrin when treated with hypochlorite of lime, and ternitracetonitrile, $C^4X^3N$, when treated with strong nitric acid. Schischkoff has also observed that when the same acid is decomposed by zinc in presence of a mineral acid, the hydrogen eliminated from the latter is almost wholly absorbed. This reaction, together with the explosive character of the fulminurates, also points to the existence of an oxide of nitrogen in these compounds; and this being the case, the mode of formation of fulminuric acid shows that the nitro-compound must also exist in fulminic acid.

Kekulé assigns to fulminic acid the formula $C^2(NO^4)(C^2N)H^2$ or $C^2XCyH^2$ which amounts to supposing (1.) That half the carbon and half the nitrogen in fulminic acid are so arranged as to yield cyanogen-compounds under the influence of certain reagents. (2.) That the remaining half of the nitrogen exists in fulminic acid in the same form as in the so-called nitro-compounds. (3.) That the remaining half of the carbon

is so disposed as to yield in certain reactions, a body belonging to the methyl-series or a product of the decomposition thereof. — This view is supported by the following facts:

Fulminating mercury treated with chlorine gas, yields chloropicrin, gaseous chloride of cyanogen, and chloride of mercury, without any evolution of carbonic acid, according to the equation:

$$C^2XCyHg^2 + 6Cl = C^2XCl^3 + CyCl + 2HgCl.$$

When chlorine is passed into water in which fulminating mercury is immersed, the gas is rapidly absorbed, the fulminating mercury dissolves, and a yellow or sometimes bluish green oil is formed in considerable quantity. The liquid decanted from this oil gave off chloride of cyanogen when heated, and on further evaporation yielded pure chloride of mercury. The oil, when purified by washing with potash and with water, and subsequent distillation with water, exhibited the properties of chloropicrin; it was however impure and yielded by analysis 69 per cent. of chlorine, whereas the formula $C^4XCl^3$ requires only 64·75. The excess is attributed by Kekulé to the admixture of a chloride of carbon produced by the action of chlorine in excess on the chloride of cyanogen.— A similar reaction of chlorine on fulminating silver was observed by Liebig, but not minutely investigated (ix, 306). Fulminating mercury distilled with chloride of lime yields pure chloropicrin, boiling between 112° and 116°, and giving by analysis 64·93 p. c. chlorine.

Fulminating mercury treated with sulphuretted hydrogen yields sulphocyanide of ammonium and carbonic acid:

$$C^2(NO^4)CyHg^2 + 4HS = 2HgS + Cy(NH^4)S^2 + 2CO^2,$$

The liquid produced by this reaction, after being filtered and freed from excess of sulphuretted hydrogen by exposure to the air, is perfectly neutral, reddens ferric salts, gives off ammonia when treated with fixed alkalis, and when evaporated yields deliquescent sulphocyanide of ammonium. With nitrate of silver, it yields sulphocyanide of silver containing 65·84 p. c. silver (calculation 65·06). The formation of a sulphocyanide in this reaction had been previously observed (ix, 302). Gay-Lussac & Liebig, by decomposing 2·268 grm. of fulminating silver with sulphuretted hydrogen, obtained a sulphur-acid which yielded 1·86 grm. of sulphate of baryta. Now, if all the carbon in the silver-salt had passed into the form of sulphocyanogen, the quantity of sulphate of baryta obtained should have been 3·70 grm.; hence it may be inferred that only half the carbon was thus disposed of. — The formation of carbonic acid in this decomposition had not been previously observed; but Kekulé finds that when sulphuretted hydrogen is passed through boiling water in which fulminating mercury is suspended, the gas which escapes contains a considerable quantity of carbonic acid; and when the same compound is decomposed by sulphide of barium, a large quantity of carbonate of baryta is precipitated.

Schischkoff doubles the formula of fulminic acid and regards it as a compound of 2 At. cyanic acid with 1 At. nitracetonitrile:

$$C^6N^4H^4O^8 = (C^2NHO^2)^2.NC^4H^3X.$$

In like manner, he regards fulminuric acid $C^6N^3H^3O^6$ as $C^2NHO^2.NC^4H^3X$, and supposes it to be derived from fulminic acid by abstraction of 1 At. cyanic acid (x, 556). When the yellow precipitate formed by the action of chloride or iodide of potassum on fulminating mercury

(x, 542) is treated with iodide of potassium, ammonia is evolved and the filtered liquid contains a cyanate, or at all events a carbonate, arising from the decomposition of the cyanate if the action has been carried too far.

Kekulé, on the other hand, maintains that fulminuric acid must have a more complex constitution than fulminic acid, because fulminating mercury treated with bromine yields bibromonitracetonitrile without evolution of carbonic acid, whereas the formation of the same compound by the action of bromine on fulminurate of potash is attended with evolution of carbonic acid. He represents the formation of fulminuric from fulminic acid by the equation:

$$2C^4N^2H^2O^4 + 2HO = C^6N^3H^3O^6 + 2CO^2 + NH^3.$$

According to Schishkoff's formula of fulminic acid, only $\frac{1}{4}$ of the nitrogen is in the form of $NO^4$, whereas according to Kekulé's formula, one-half of the nitrogen is in that form. Now, as the nitrogen of nitro-compounds is never completely converted into ammonia by burning with soda-lime, it follows that if Kekulé's view be correct, fulminating mercury burnt with soda-lime should yield only half its nitrogen, that is to say 4·9 per cent. in the form of ammonia, whereas, according to Schishkoff's formula, $\frac{3}{4}$ of the nitrogen, or 7·4 per cent., should be thus given off. Now Kekulé obtained in two experiments 6·29 and 6·21 p. c. nitrogen, a result which is not easily explained on Schischkoff's view, inasmuch as the nitrogen even of nitro-compounds is always partly converted into ammonia by combustion with soda-lime, and therefore the error should be rather in excess than in defect.

According to Kekulé's formula, fulminic acid belongs to the same type as marsh-gas, and exhibits a very close analogy with the bodies in the following series:

| | | | | | | |
|---|---|---|---|---|---|---|
| Marsh gas | $C^2$ | H | H | H | H. | |
| Chloride of Methyl | $C^2$ | H | H | H | Cl. | |
| Chloroform | $C^2$ | H | Cl | Cl | Cl. | |
| Nitroform | $C^2$ | H | X | X | X. | |
| Chloropicrin | $C^2$ | X | Cl | Cl | Cl. | |
| Marignac's Oil (vii, 360) | $C^2$ | X | X | Cl | Cl. | |
| Acetonitrile | $C^2$ | H | H | H | Cy | = $C^4H^3N$. |
| Terchloracetonitrile | $C^2$ | Cl | Cl | Cl | Cy | = $C^4Cl^3N$. |
| Ternitracetonitrile | $C^2$ | X | X | X | Cy | = $C^4X^3N$. |
| Bibromonitracetonitrile | $C^2$ | X | Br | Br | Cy | = $C^4X\,Br^2N$. |
| Fulminating Mercury | $C^2$ | X | Hg | Hg | Cy | = $C^2XHg^2N$. |
| Fulminic acid (*hyp.*) | $C^2$ | X | H | H | Cy | = $C^2XH^2N^2$. |

According to these formulæ, the compounds to which fulminic acid is most intimately related are chloropicrin and acetonitrile; its formula is in fact the same as that of mononitracetonitrile.

The formation of fulminic acid by the action of nitric acid upon alcohol may be explained as follows. On the one hand, cyanic acid is formed:

$$C^4H^6O^2 + 2NO^3 = 2C^2NHO^2 + 4HO;$$

on the other, nitro-acetic acid; and these two compounds by their mutual action produce fulminic acid:

$$C^4H^3XO^4 + C^2NHO^2 = C^4H^2XN + 2CO^2 + 2HO;$$

or, according to Schishkoff:

$$C^4H^3XO + 3C^2NHO^2 = (C^2NHO^2)^3.NC^4H^2X + 2CO^2 + 4HO.$$

Kekulé regards the formation of fulminating mercury as analogous to that of chloroform. In the one case, alcohol is subjected to the simultaneous action of oxidising and chlorinising agents; in the other, the alcohol is likewise oxidised [converted into cyanic acid], while at the same time, cyanogen and mercury are present and ready to take the place which the chlorine occupies in chloroform, the strong nitric acid likewise introducing the group $NO^4$. In fact, fulminating mercury might be regarded as nitrated chloroform, in which 2 At. Cl are replaced by mercury and one by cyanogen. This view receives some corroboration from the fact that the analogous compound, chloropicrin, is produced by adding chloride of sodium to a mixture of alcohol and strong nitric acid.

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## Methyl-thialdine.

$C^{14}H^{15}NS^4 = C^{12}NH^{12}(C^2H^3)$.

A. W. Hofmann. *Chem. Soc. Qu. J.* 10, 193.

When thialdine is dissolved in iodide of methyl mixed with its own bulk of ether, a solid crystalline mass is formed after 12 hours, consisting of hydriodate of methyl-thialdine, which may be freed from adhering thialdine by washing with ether and crystallising from alcohol. The mixture must not be heated, as in that case it becomes brown and resinous.

| | | | Hofmann. |
|---|---|---|---|
| 14 C | 84 | 27·53 | 26·92 |
| 16 H | 16 | 5·25 | 5·44 |
| N | 14 | 4·59 | |
| 4 S | 64 | 20·98 | |
| I | 127 | 41·65 | |
| $C^{14}H^{15}NS^4,HI$ | 305 | 100·00 | |

The salt is soluble in water and alcohol, but insoluble in ether, which precipitates it in the crystalline state from the alcoholic solution. The aqueous solution has an acid reaction, and when mixed with potash in the cold, deposits the salt in its original state. These characters resemble those of the iodides of the ammonium-bases, such as iodide of tetramethylium. The compound is however somewhat less soluble in water than might be expected if it were constituted in that manner, and moreover undergoes complete decomposition when boiled with a caustic alkali; whereas iodide of tetramethylium may be recrystallised unchanged from a strong boiling solution of potash.

On adding oxide of silver to a solution of the hydriodate or iodide of methylthialdine, iodide of silver is formed, and the liquid acquires a strong alkaline reaction, perhaps from separation of a fixed base; but a further decomposition instantly ensues; sulphide of silver is formed;

aldehyde is evolved in considerable quantity; and the liquid is found to contain ammonia, oxide of tetramethylium and acetate of silver:

$$4C^{14}H^{16}NS^4I + 20AgO + 5HO = \underbrace{C^6H^{12}NO}_{\text{oxide of tetramethylium.}} + \underbrace{12C^4H^4O^2}_{\text{aldehyde.}} + 3NH^3 + 16AgS + 4AgI.$$

The acetic acid is a further product of the oxidation of the aldehyde.

As thialdine has been stated to be converted into leucine $C^{12}H^{13}NO^4$ by the action of oxide of silver (ix, 314), it appeared probable that a homologous compound, namely, methyl-leucine, would be found among the products of the decomposition of methylthialdine by oxide of silver. No such compound was however observed. Moreover, Hofmann has shown by direct experiment that when thialdine is decomposed by oxide of silver, the *whole* of the nitrogen is eliminated in the form of ammonia, and not a trace of leucine or any other nitrogenous organic compound is produced. 2·065 grm. of thialdine were desulphurised by oxide of silver; and the liquid freed from silver by hydrochloric acid, was mixed with bichloride of platinum; chloroplatinate of ammonium was thus obtained, weighing 2·792; by calculation, supposing all the nitrogen to be converted into ammonia, it should have been 2·828. In another experiment, 0·317 grm. thialdine yielded 0·430 grm. chloroplatinate of ammonia, the quantity required by calculation being 0·436 grm. Hence it appears that the original statement of Liebig & Wöhler (ix, 313) respecting the decomposition of thialdine by oxide (or nitrate) of silver, is correct.

Iodide of *ethyl* acts on thialdine in the same manner as iodide of methyl, but the crystalline iodide forms more slowly. The formation of the corresponding *amyl*-compound requires several weeks.

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## Binitro-ethylic Acid. $C^4H^6N^2O^4$.

FRANKLAND. *Phil. Trans.* 1857, 59; *Ann. Pharm.* 99, 342; *Chem. Soc. Qu. J.* 11, 89.

***Dinitroethylic acid.***

*Formation and Preparation.* If a small quantity of zincethyl, either pure or dissolved in ether, be passed up into dry binoxide of nitrogen confined over mercury, the binoxide is very slowly but completely absorbed in large quantity, without the production of any other gas. The solution may be accelerated by agitation, but even then it is exceedingly slow. At the expiration of from one to four days, rhomboidal crystals begin to be deposited, and increase in number until the liquid finally solidifies.

To prepare these crystals in larger quantity, about an ounce of zincethyl, dissolved in an equal bulk of dry ether, is placed in a flat-bottomed flask and supplied with binoxide of nitrogen from a gas-holder, the gas being thoroughly dried by passing through a long series of bulbs filled with concentrated sulphuric acid, which also serves to absorb any traces of nitrous gas that might be formed by atmospheric oxygen gaining access to the interior of the apparatus. The gas is conducted into the flask by a tube which terminates just below the cork, a provision being made for its exit by another tube continued to within a short distance of the surface of the liquid, and terminating outside the cork in a capil-

lary extremity, which can be readily sealed up by the blowpipe and reopened at pleasure. As binoxide of nitrogen prepared from copper turnings and nitric acid, always contains a considerable percentage of protoxide, it is necessary occasionally to allow a stream of the gas to flow through the flask, so as to prevent the absorption being hindered or stopped by the accumulation of protoxide of nitrogen: at other times the exit tube is hermetically sealed, and the gas supplied only as it is absorbed. The absorption is however extremely slow, requiring several weeks to complete it, even when the operation is continued day and night, and a fortnight, even when the action is accelerated by violent agitation for several hours each day. It may however be greatly accelerated by introducing the zinc-ethyl into a strong copper cylinder furnished with a condensing syringe, by which the binoxide of nitrogen may be compressed to about 20 atmospheres.* By this condensation, aided by agitation of the liquid, the process may be completed within a day.

The crystalline compound obtained by this process is a compound of binitro-ethylate of zinc with zinc-ethyl, its formation being represented by the equation:

$$2C^4H^5Zn + 2NO^2 = C^4H^5ZnN^2O^4,C^4H^5Zn.$$

It is decomposed by water, with evolution of hydride of ethyl and formation of basic binitroethylate of zinc, which remains dissolved in the water, forming a milky solution:

$$C^4H^5ZnN^2O^4,C^4H^5Zn + HO = C^4H^5,H + C^4H^5ZnN^2O^4,ZnO,$$

and on passing carbonic acid through this liquid, carbonate of zinc is precipitated, and a solution is obtained which when evaporated to dryness yields neutral binitroethylate of zinc in the form of a radiated crystalline mass composed of $2C^4H^5ZnN^2O^4$ + Aq.; this when heated to 100°, yields the anhydrous salt $C^4H^5ZnN^2O^4$.

*Binitroethylic acid.*—When dry binitroethylate of zinc is treated with concentrated sulphuric acid, and the vessel containing those ingredients is placed in a freezing mixture, binitroethylic acid is liberated; but it is so unstable, that when the temperature rises a few degrees, it begins to effervesce violently, and is rapidly decomposed with evolution of gases and white vapours. A dilute solution is somewhat more stable; it may be prepared either by decomposing a dilute solution of binitroethylate of zinc with dilute sulphuric acid, and then distilling in vacuo, or by adding to a dilute solution of the baryta-salt just sufficient sulphuric acid to precipitate the base. Dilute binitroethylic acid thus prepared possesses a pungent odour, somewhat resembling that of the nitro-fatty acids, and an acid taste. It reddens litmus paper strongly, and gradually decomposes, even at ordinary temperatures.

The hypothetical anhydrous acid $C^4H^5N^2O^3$, may be regarded as belonging to the type of nitric oxide containing a double atom of nitrogen ($N^2O^4$) and having 1 At. oxygen replaced by ethyl thus: $N^2\left\{\begin{matrix}C^4H^5\\O^3\end{matrix}\right.$ or as nitrous acid ($NO^3$) having 1 At. oxygen replaced by ethyl and another by nitric oxide: $N\left\{\begin{matrix}C^4H^5\\NO^2\\O\end{matrix}\right.$

* For a figure and description of the apparatus, see the original memoir in either of the Journals above referred to.

The salts of binitroethylic acid are all soluble in water and alcohol, and most of them crystallise with more or less difficulty. They are all violently acted upon by concentrated nitric acid, the binitroethylic acid being entirely decomposed and a nitrate of the constituent base produced. Dilute nitric acid acts in the same manner, but more slowly. They all fuse at a temperature a little above 100°. The potash, soda, lime, and baryta-salts deflagrate explosively, like loose gunpowder, at a temperature considerably below redness.

*Binitroethylate of Soda.* — Prepared by precipitating binitroethylate of lime with carbonate of soda, and evaporating the filtrate in a water-bath. The residue being treated with strong alcohol, the binitroethylate of soda dissolves, and is thus separated from the excess of carbonate of soda. The alcoholic solution evaporated to dryness in a water-bath, yielded minute scaly crystals, which were anhydrous.

| | | | Frankland. |
|---|---|---|---|
| 4 C | 24 | 21·43 | |
| 5 H | 5 | 4·46 | |
| 2 N | 28 | 25·00 | 25·46 |
| NaO | 31 | 27·68 | 27·60 |
| 3 O | 24 | 21·43 | |
| $C^4H^5NaN^2O^4$ | 112 | 100·00 | |

*Binitroethylate of Baryta.* — This salt is produced by adding caustic baryta in excess to a solution of binitroethylate of zinc, carbonic acid being passed through the solution until the excess of baryta is precipitated. It is then treated with sulphuretted hydrogen to remove a trace of oxide of zinc, which is still held in solution. After being heated to boiling for a few minutes, and then filtered, the solution is concentrated by evaporation, and finally dried down to a gummy mass, which does not crystallise on cooling. This is anhydrous binitroethylate of baryta. It is uncrystallisable, very deliquescent, and very soluble in water. Its solution is perfectly neutral to test-paper.

| | | | Frankland. |
|---|---|---|---|
| 4 C | 24·0 | 15·23 | 14·65 |
| 5 H | 5·0 | 3·17 | 3·28 |
| 2 N | 28·0 | 17·77 | |
| Ba | 68·6 | 43·52 | 43·82 |
| 4 O | 32·0 | 20·31 | |
| $C^4H^5BaN^2O^4$ | 157·6 | 100·00 | |

*Binitroethylate of Lime,* $C^4H^5CaN^2O^4 + 3Aq$. — This salt is readily prepared by treating a solution of binitroethylate of zinc with excess of hydrate of lime, passing carbonic acid through the solution, and then boiling for a few minutes. The filtered solution deposits, on evaporation, beautiful silky needles of binitroethylate of lime, which contain three atoms of water, two of which are expelled at 100° C. An estimation of lime in this salt gave 20·76 per cent.; the above formula requires 20·59 per cent.

When this salt in the state of coarse powder is exposed to the gradual action of strong sulphuric acid, in a vessel externally cooled, a quantity of gas is evolved, equal in weight to 30·6 per cent. of the salt, that is to say, almost exactly half that of the anhydrous acid contained in it

(59·6 p. c.). The gaseous mixture thus evolved had a sp. gr. of 1·3601 and contained in 100 pts. 8·90 pts. of nitric oxide, 24·24 of olefiant gas, 60·65 of nitrous oxide, and 6·21 of nitrogen. The liquid and solid products of the decomposition contained sulphate of lime, sulphovinate of lime, and sulphate of ammonia or ethylamine.

*Binitroethylate of Magnesia.* — Prepared by treating the solution of binitroethylate of zinc with excess of caustic magnesia, boiling and filtering. The filtered solution, concentrated in a water-bath, yields granular crystals, which fuse at 100°, and dry up to a solid amorphous mass consisting of the anhydrous salt.

| | | | Frankland. |
|---|---|---|---|
| 4 C | 24 | 23·76 | |
| 5 H | 5 | 4·95 | |
| 2 N | 28 | 27·72 | 29·37 |
| MgO | 20 | 19·80 | 19·92 |
| 3 O | 24 | 23·77 | |
| $C^4H^5MgN^2O^4$ | 101 | 100·00 | |

*Binitroethylate of Zinc.* — *a. Basic.* — $C^4H^5ZnN^2O^4,ZnO$. — Produced by the action of water on binitroethylate of zinc and zinc-ethyl (p. 556); also by exposing that compound to a stream of dry air, whereby neutral binitroethylate of zinc and ethylate of zinc are formed, and treating the product with water:

$$C^4H^5ZnN^2O^4,C^4H^5Zn + 2O = C^4H^5ZnN^2O^4 + C^4H^5ZnO^2.$$

and:

$$C^4H^5ZnN^2O^4 + C^4H^5ZnO^2 + HO = C^4H^5ZnN^2O^4,ZnO + C^4H^6O^2.$$

*b. Neutral.* — $C^4H^5ZnN^2O^4$. — *Preparation* (p. 556). — Crystallises in minute colourless needles containing half an equivalent of water, which they retain when exposed over sulphuric acid *in vacuo*. They melt below 100°, and gradually become anhydrous at this temperature. They are very soluble in water and in alcohol. The concentrated aqueous solution solidifies on cooling to a white fibrous crystalline mass. Heated suddenly in air to a temperature of about 300°, this salt does not deflagrate, but inflames, burning rapidly with a beautiful bluish green flame.

| | *Dried at* 100°. | | Frankland. |
|---|---|---|---|
| 4 C | 24·0 | 19·75 | 19·87 |
| 5 H | 5·0 | 4·11 | 4·41 |
| 2 N | 28·0 | 23·04 | |
| Zn | 32·5 | 26·76 | 27·29 |
| 4 O | 32·0 | 26·34 | |
| $C^4H^5ZnN^2O^4$ | 121·5 | 100·00 | |

| | *Crystallised.* | | Frankland. |
|---|---|---|---|
| 8 C | 48 | 19·04 | 18·70 |
| 11 H | 11 | 4·36 | 4·68 |
| 4 N | 56 | 22·22 | 23·78 |
| 2 Zn | 65 | 25·81 | 25·46 to 26·23 |
| 9 O | 72 | 28·57 | |
| $2C^4H^5ZnN^2O^4 + Aq$ | 252 | 100·00 | |

*Binitroethylate of Zinc with Zincethyl.* — $C^8H^{10}Zn^2N^2O^4 = C^4H^5ZnN^2O^4 + C^4H^5Zn$. — *Preparation* (p. 556). — It is also obtained by adding an ethereal solution of zincethyl to anhydrous binitroethylate of zinc. — Corresponding compounds appear to be formed in like manner with other salts of binitroethylic acid: these compounds are analogous to the compound of zincethyl with iodide of zinc, which is formed so abundantly during the preparation of zincethyl.

Binitroethylate of zinc and zincethyl is deposited from its ethereal solution in large colourless and transparent rhomboidal crystals, which instantly become opaque on exposure to the air, owing to the formation of an oxidised product.

| | | | Frankland.* |
|---|---|---|---|
| 8 C | 48 | 26·22 | 25·61 |
| 10 H | 10 | 5·46 | 5·48 |
| 2 N | 28 | 15·30 | 14·89 |
| 2 Zn | 65 | 35·53 | 35·36 |
| 4 O | 32 | 17·49 | 18·46 |
| $C^4H^5ZnN^2O^4,C^4H^5Zn$ | 183 | 100·00 | 100·00 |

The simplest expression of the analytical results is $C^4H^5ZnNO^2$, which represents the salt as composed of 1 At. zinc-ethyl and 1 At. nitric oxide; but the decomposition of the salt by oxidation and by the action of water (p. 556), seem to show that its true formula is that above given.

The crystals dissolve with tolerable facility and without decomposition in anhydrous ether, but are instantly decomposed by anhydrous alcohol and by water. The compound exposed to the gradually increasing heat of an oil-bath, melts at 100°, then froths up and begins slowly to evolve gas. At 180°, the colour darkens, and a small quantity of a yellowish liquid of penetrating odour, free from zincethyl, and possessing a very powerful alkaline reaction, distils over. This liquid, neutralised with hydrochloric acid and treated with bichloride of platinum, yielded a splendidly crystalline platinum salt, which was obtained, however, in too small quantity to allow of its composition being determined. From 180° to 190°, binitroethylate of zinc and zincethyl rapidly evolves gas consisting of 18·4 per cent. carbonic acid, 23·66 per cent. olefiant gas, and 57·94 per cent. of a mixture of hydride of ethyl, nitrogen, and protoxide of nitrogen.

*Binitroethylate of Copper.* — This salt is prepared by mixing solutions of binitroethylate of baryta and sulphate of copper. The filtered solution is of a magnificent purple colour; on evaporation *in vacuo*, it yields splendid purple needles, which contain half an equivalent of water, and may be obtained several inches in length; they are four-sided prisms.

| | | | Frankland. |
|---|---|---|---|
| 8 C | 48·0 | 19·18 | 19·60 |
| 11 H | 11·0 | 4·39 | 3·93 |
| 4 N | 56·0 | 22·37 | 21·82 |
| 2 CuO | 79·3 | 31·68 | 31·12 |
| 7 O | 56·0 | 22·38 | 23·53 |
| $2C^4H^5CuN^2O^4 + Aq$ | 250·3 | 100·00 | 100·00 |

* In this and in the analysis of the other salts, the mean of the experimental numbers is given.

*Binitroethylate of Silver* is produced by double decomposition from binitroethylate of baryta and sulphate of silver. It is very soluble in water, crystallizes in very light scales, and is so speedily decomposed, even with little exposure to light, that no satisfactory analysis could be made of it.

*Double Nitrate and Binitroethylate of Silver.* — This salt is very sparingly soluble in water; it is precipitated in a crystalline granular form when concentrated solutions of binitroethylate of zinc and nitrate of silver are mixed.

| | | | | Frankland. |
|---|---|---|---|---|
| 4 C | 24 | | 6·54 | 6·67 |
| 5 H | 5 | | 1·36 | 1·44 |
| 3 N | 42 | | 11·45 | |
| 2 Ag | 216 | | 58·86 | 58·89 |
| 10 O | 80 | | 21·79 | |
| $C^4H^5AgN^2O^4 + NO^5Ag$ | 367 | | 100·00 | |

*Binitroethylic Ether.* — Several attempts were made to prepare this compound by the usual methods of etherification, but with only very partial success. When crystallized binitroethylate of lime is distilled with sulphovinate of potash, alcohol comes over mixed with an ethereal liquid, which dissolves in water, but separates again on the addition of chloride of calcium, in the form of oily drops of a peculiar ethereal odour. The quantity was however so small as to preclude the possibility of fixing its composition.

END OF VOL. XII.

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